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SELF-CONSISTENT FIELD SCHEMES FOR THE TWO-ELECTRON
ATOMIC IONS IN THE GROUND STATE

by

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TABLE OF CONTENTS

ABSTRACT	ii
ACKNOWLEDGEMENTS	iv
INTRODUCTION	1
I. PHYSICAL INTERPRETATION OF SOME SELF-CONSISTENT FIELD MODELS	3
II. GENERALIZED SELF-CONSISTENT FIELD SCHEMES	10
III. PERTURBATION THEORY	19
IV. PERTURBATION EXPANSION OF THE SELF-CONSISTENT FIELD EQUATIONS FOR THE TWO-ELECTRON ATOMIC IONS	29
V. THE ZERO-ORDER EXTENDED HARTREE-FOCK ORBITALS	43
VI. NUMERICAL SOLUTION OF THE FIRST-ORDER EXTENDED HARTREE-FOCK EQUATIONS	55
VII. DISCUSSION OF THE RESULTS	61
APPENDIX I. THE NATURAL ORBITALS OF TWO-ELECTRON WAVE FUNCTIONS	64
APPENDIX II. PHYSICAL INTERPRETATION OF THE SELF- CONSISTENT FIELD SCHEMES	70
APPENDIX III. CONCERNING THE SIGN OF THE FIRST-ORDER NATURAL OCCUPATION AMPLITUDES	74
APPENDIX IV. CALCULATION OF THE MATRIX ELEMENTS	77
APPENDIX V. COEFFICIENTS OF SOME ZERO-ORDER BASIC EXTENDED HARTREE-FOCK ORBITALS	90

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by

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ABSTRACT

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The formalism for the generalized N-configuration self-consistent (SCF) schemes is developed for the two-electron atomic ions in the ground state. The equations for the SCF orbitals are expanded in powers of the inverse nuclear charge according to the well-known perturbation scheme based on considering the electronic interaction potential as a perturbation. Several first-order SCF equations are solved numerically.

The formalism for the exact wave function is cast into SCF form by writing it in terms of the natural orbitals. Each natural orbital is considered as a function of an infinite number of parameters which are generalizations of the natural occupation amplitudes. The formalism for any N-configuration SCF scheme is obtained from the natural orbital formalism by setting all but the first N parameters equal to zero. The k-th N-configuration SCF orbital is thus the k-th natural orbital with all but the

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first N natural occupation amplitudes set equal to zero. The N -configuration SCF wave function is a generalization of the ordinary Restricted Hartree-Fock wave function and is the best possible N -configuration wave function.

The perturbation expansion of the N -configuration SCF schemes is effected by first developing the exact problem in terms of the inverse nuclear charge, transforming the exact problem into natural orbital form and then setting the appropriate parameters equal to zero. The natural occupation amplitudes are divided into the intrinsic and the correlation amplitudes. The intrinsic amplitudes can never be zero, while the correlation amplitudes go to zero as the inverse nuclear charge goes to zero. The natural orbitals are divided into intrinsic and correlation orbitals by their association with the occupation amplitudes. The first-order equations define only the zero-order correlation orbitals.

The first-order part of the Extended Hartree-Fock (EHF) scheme, defined as that SCF scheme which contains one correlation orbital of each angular symmetry type, is discussed in detail. The double-excitation parts of several second-order EHF energies are obtained numerically and compare very favorably with the exact values. These second-order energies are the lowest possible energies obtainable from an orbital product approximation to the double-excitation part of the exact first-order wave function.

A handwritten signature in black ink, appearing to be 'P. H. P.', is located in the bottom right corner of the page.

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INTRODUCTION

The exact wave function of a quantum-mechanical system is a function of the spatial and spin coordinates of all the electrons. The wave function does not assign electrons to orbitals and does not factor into products of simpler functions. Such a complicated functional form is necessary in order to adequately describe the correlation between the electrons. The correlation arises because electrons repel each other and thus adjust their motions and spatial distributions so as to stay as far apart as possible. An exact many-electron wave function is difficult to calculate and can be obtained only approximately. It would therefore be desirable to replace the exact problem by a more tractable model.

A very successful model has been the restricted Hartree-Fock (RHF) model.^{1,2} This model assigns each electron to an orbital in such a way that two closed-shell electrons occupy similar spatial orbitals but with different spins. The RHF model, however, neglects electron correlation.³ Lowdin has suggested that some portion of the correlation can be taken into account by allowing every electron to occupy a different space orbital.⁴ If these orbitals are restricted to be s-type orbitals, the model is the "different orbitals for different spins" (DODS) model. If the angular dependence of the orbitals is not restricted, the model is the extended Hartree-Fock (EHF) model. The RHF, DODS and EHF models are self-consistent field (SCF) schemes in that the equations for the various functions are nonlinear integro-differential equations.

Variational calculations of several DODS and EHF energies⁵⁻⁷ have yielded values considerably lower than the RHF values.

The aim of this work is to set up, investigate and evaluate an SCF approach to the two-electron atomic problem. The discussion will be limited to the ground states of the two-electron atomic ions. The investigation will begin with some discussion of the intuitive derivation of the RHF and DODS schemes. In Section II a hierarchy of generalized SCF schemes will be formally derived from the exact problem. In Section III the exact problem will be developed according to a perturbation scheme which treats the electronic interaction as a perturbation. The results of Section III will be used to guide the way in developing the generalized SCF schemes according to the above-mentioned perturbation method. In Section V a particular set of (perturbed) SCF orbitals, the EHF orbitals, will be discussed, and in Section VI the numerical solution of the first-order EHF perturbation equations will be investigated. The work will be concluded with Section VII in which the possible virtues of SCF methods for two-electron atomic systems will be discussed.

The original contributions of this work can be summarized as follows: (1) The coupled, integro-differential equations for a general SCF scheme have been derived, and the RHF, DODS and EHF schemes have been put into a perspective with respect to all possible SCF schemes; (2) The similarities, differences and connection of all possible SCF orbitals with each other and with the natural spin orbitals of Lowdin have been established; (3) The perturbation expansion of the general SCF equations in powers of the inverse

nuclear charge has been set up; (4) Several first-order EHF perturbation equations have been solved numerically and several second-order EHF energies have been obtained.

I. PHYSICAL INTERPRETATION OF SOME SELF-CONSISTENT FIELD MODELS

The RHF and DODS models are intuitively appealing in that they assign each electron to a separate orbital. Before discussing these models, however, some orientation is necessary. In any discussion in this work the Hamiltonian referred to will always be the exact, non-relativistic, spin-free, two-electron Hamiltonian $H(\mathbf{r}_1, \mathbf{r}_2)$ given by

$$H(\mathbf{r}_1, \mathbf{r}_2) = h(\mathbf{r}_1) + h(\mathbf{r}_2) + \frac{1}{Z} \frac{1}{r_{12}}, \quad (1.1)$$

where $h(\mathbf{r})$ is the ordinary hydrogenic Hamiltonian

$$h(\mathbf{r}) = -\frac{1}{2} \nabla^2 - \frac{1}{r}, \quad (1.2)$$

where $\frac{1}{r_{12}}$ represents the electronic interaction potential and where Z is the nuclear charge of the ion. The symbol \mathbf{r}_i denotes the collection of the three spatial coordinates of the i -th electron. All distances are in units of a_0/Z , and all energies are in units of $Z^2 e^2/a_0$ where e is the electronic charge and where $a_0 = \hbar^2/\mu e^2$ with μ the reduced mass of the electron.

The crudest possible model, which will be called the zero-order model, is obtained by assuming that the spatial distribution of each

electron is the same distribution which would exist if the electronic interaction potential were neglected. Such a model predicts that each electron occupies a hydrogenic orbital. The ground state has both electrons occupying the $1s$ hydrogenic space orbital, one electron with α spin and one electron with β spin. The zero-order spatial wave function will be denoted by $\Psi^{(0)}(r_1, r_2)$ where

$$\Psi^{(0)}(r_1, r_2) = 1s(r_1) 1s(r_2). \quad (1.3)$$

The spin has been factored out and neglected. The designation "wave function" is reserved for any two-electron function which describes a state of the two-electron system. The designation "orbital" is applied to any one-electron function which might be a wave function for a single electron. The $1s$ hydrogenic orbitals are s-type functions in that each one is a product of a radial function and the spherical harmonic $Y_0^0(\theta, \phi)$ equal to $1/\sqrt{4\pi}$. The energy of the two-electron ions which the zero-order model predicts is obtained by taking the expectation value of the Hamiltonian with respect to the zero-order wave function. For the case of the helium atom the energy predicted by the zero-order model is $-2.75 e^2/a_0$ as compared with the non-relativistic value⁸ of $-2.9037244 e^2/a_0$. In all further discussions, the unit of energy e^2/a_0 will be called an atomic unit (a.u.) of energy.

The simplest improvement over the zero-order model is offered by the RHF model. This model, just like the zero-order one, assigns each (ground-state) electron to one space orbital but requires that

this orbital be the energetically optimum orbital. The RHF wave function has the same form as the zero-order wave function, i.e.

$$\Psi_{RHF}(\zeta_1, \zeta_2) = u(\zeta_1) u(\zeta_2). \quad (1.4)$$

The RHF orbital $u(\zeta)$ is required to be an s-function just like the hydrogenic 1s orbital. The RHF energy, just like the energy of the zero-order model, is obtained by taking the expectation value of the Hamiltonian with respect to the RHF wave function. In terms of the RHF orbital u the RHF energy is

$$E_{RHF} = 2 \langle u | h | u \rangle + \frac{1}{2} \langle u u | \frac{1}{r_{12}} | u u \rangle \quad (1.5)$$

with

$$1 = \langle u | u \rangle. \quad (1.6)$$

The equation for the RHF orbital⁹ is obtained by requiring E_{RHF} to be stationary with respect to variations in u subject to the normalization constraint, eq. (1.6). The equation is

$$\left[h_0(r_1) + \frac{1}{2} \langle u(r_2) | \frac{1}{r_2} | u(r_2) \rangle_{r_2} - \epsilon \right] u(r_1) = 0 \quad (1.7)$$

where r_2 is the greater of r_1 and r_2 , where the parameter ϵ is

$$\epsilon = E_{RHF} - \langle u | h_0 | u \rangle \quad (1.8)$$

and where the operator $h_0(r)$ is

$$h_0(r) = -\frac{1}{2r} \frac{\partial^2(r)}{\partial r^2} - \frac{1}{r}. \quad (1.9)$$

The quantity $\langle u(r_2) | \frac{1}{r_2} | u(r_2) \rangle_{r_2}$ is the average electron interaction defined to be

$$\langle u(r_2) | \frac{1}{r_2} | u(r_2) \rangle_{r_2} = \int_0^\infty dr_2 r_2^2 u(r_2) \frac{1}{r_2} u(r_2). \quad (1.10)$$

The function $u(r)$ is the radial part of the RHF orbital $u(r)$. For the case of the helium atom the ground-state RHF energy¹⁰ is -2.861680 a.u. The reason for the inaccuracy in this energy is because, even though the RHF wave function is the best single configuration wave function, a single configuration is not sufficient to describe electron correlation.

The RHF wave function (for the ground state) is not at all correlated. The probability of finding one electron about the point \mathbf{r}_1 and the other electron simultaneously about the point \mathbf{r}_2 (the absolute square of the wave function) is just the product of two independent probabilities. The RHF approximation (for singlet states) just like any SCF model neglects the Coulomb hole³ about each electron since the probability of finding both electrons at the same point in space is not zero.

Some (radial) correlation is taken into account by the DODS model. The DODS wave function has the form

$$\Psi_{\text{DODS}}(\kappa_1, \kappa_2) = \frac{1}{\sqrt{2}} [\psi(\kappa_1)\chi(\kappa_2) + \chi(\kappa_1)\psi(\kappa_2)] \quad (1.11)$$

which is a generalization of the RHF wave function. If the DODS orbitals ψ and χ are restricted to be equal to each other, one would then have the RHF wave function. The DODS orbitals are s-functions and are defined to be the energetically optimum orbitals. The DODS energy, obtained by taking the expectation value of the Hamiltonian with respect to the DODS wave function, is

$$E_{\text{DODS}} = \frac{\begin{aligned} &\langle \psi | h | \psi \rangle + \langle \chi | h | \chi \rangle \\ &+ 2 \langle \psi | h | \chi \rangle \langle \psi | \chi \rangle \\ &+ \frac{1}{2} \langle \psi \chi | \frac{1}{r_{12}} | \psi \chi \rangle + \frac{1}{2} \langle \psi \chi | \frac{1}{r_{12}} | \chi \psi \rangle \end{aligned}}{1 + \langle \psi | \chi \rangle^2} \quad (1.12)$$

with the conditions

$$\langle \psi | \psi \rangle = 1 \quad (1.13a)$$

and

$$\langle \chi | \chi \rangle = 1. \quad (1.13b)$$

The two equations¹¹ for ψ and χ are obtained by requiring E_{DODS} to be stationary with respect to variations in ψ and χ subject to the normalization constraints, eqs. (1.13).

The equations are

$$\begin{aligned} & \left[h_0(r_1) + \frac{1}{Z} \langle \chi(r_2) | \frac{1}{r_2} | \chi(r_2) \rangle_{r_2} - \epsilon_{\psi\psi} \right] \psi(r_1) \\ & + \left[\langle \psi | \chi \rangle h_0(r_1) + \frac{1}{Z} \langle \chi(r_2) | \frac{1}{r_2} | \psi(r_2) \rangle_{r_2} - \epsilon_{\psi\chi} \right] \chi(r_1) = \\ & = 0 \quad (1.14a) \end{aligned}$$

and

$$\begin{aligned} & \left[h_0(r_1) + \frac{1}{Z} \langle \psi(r_2) | \frac{1}{r_2} | \psi(r_2) \rangle_{r_2} - \epsilon_{\chi\chi} \right] \chi(r_1) \\ & + \left[\langle \psi | \chi \rangle h_0(r_1) + \frac{1}{Z} \langle \chi(r_2) | \frac{1}{r_2} | \psi(r_2) \rangle_{r_2} - \epsilon_{\psi\chi} \right] \psi(r_1) = \\ & = 0 \quad (1.14b) \end{aligned}$$

where the epsilons are defined as

$$\epsilon_{\psi\psi} = E_{\text{DODS}} - \langle \chi | h_0 | \chi \rangle, \quad (1.15a)$$

$$\epsilon_{\psi\chi} = \langle \psi | \chi \rangle E_{\text{DODS}} - \langle \psi | h_0 | \chi \rangle \quad (1.15b)$$

and

$$\epsilon_{\chi\chi} = E_{\text{DODS}} - \langle \psi | h_0 | \psi \rangle \quad (1.15c)$$

Since the DODS equations have not been solved, one can only say that the DODS energy for helium is below the value^{5,6} -2.8756614 a.u.

The DODS model takes radial correlation into account in an average way by pulling one electron close to the nucleus and by pushing the other one further out. The probability that one electron is about the point ζ_1 and the other electron simultaneously

about the point \mathcal{L}_2 is no longer the product of two independent probabilities but contains a cross term. Even though the two electrons can, in the DODS model, occupy the same point in space, they tend to avoid each other by occupying on the average different regions of space.

The RHF and DODS equations are all one-electron, non-linear, integro-differential equations and must be solved numerically.

However, Linderberg^{9a} and Cohen^{9b} have successfully tackled the RHF equation by a perturbation method. The electronic interaction potential $1/r_{12}$ was considered as a perturbation, and the RHF orbital and RHF energy were expanded in powers of the inverse nuclear charge $1/Z$. The first-order RHF equations were easily integrated to obtain the first-order RHF orbital.

It was hoped that the same perturbation method of solution could be applied to the DODS equations. However, in expanding the DODS orbitals in terms of the inverse nuclear charge, it turned out that the only first-order solution to the DODS equations was just the first-order RHF orbital. Thus, in using the inverse nuclear charge as a perturbation parameter, the DODS equations collapsed into the RHF equation. The clue to the reason for the collapse was pointed out by Professor Byers Brown. After analyzing in powers of $1/Z$ the variational DODS wave functions of Shull and Löwdin⁵ he pointed out that one must use the square root of the inverse nuclear charge $1/\sqrt{Z}$ as the perturbation parameter for the DODS equations. The necessity of using the square root of the inverse nuclear charge instead of the nuclear charge itself as the expansion parameter has

been subsequently discussed by Stewart¹² and by Coulson.¹¹ As it will be shown in Section IV, one avoids the necessity of introducing $1/\sqrt{Z}$ into the discussion if the problem is set up in natural orbital form. By rewriting the DODS formalism, a perturbation expansion involving only $1/Z$ can be defined.

The RHF wave function is the best single-configuration wave function, and the DODS wave function is the best two-configuration wave function. One can go on and formulate the equations for the best N-configuration wave function. Instead of considering a particular SCF scheme, the general N-configuration SCF scheme will be discussed. In the next section a hierarchy of SCF functions will be derived. The lowest two members of the hierarchy will be the RHF and DODS wave functions, and the highest member will be the exact wave function.

II. GENERALIZED SELF-CONSISTENT FIELD SCHEMES

A generalized N-configuration SCF scheme is such a scheme which gives the best approximate wave function consisting of N configurations. The generalized SCF schemes for the ground state will be developed as members of a hierarchy of SCF schemes. The lowest member of the hierarchy is the RHF scheme and the highest member the exact problem.

In trying to obtain the exact wave function of a system $\Psi(r_1, r_2)$ it is customary to expand it in some suitable (finite) set of known, ortho-normal, one-electron functions with unknown coefficients. Choosing different sets of functions leads to different

coefficients and thus to different representations of the same wave function. There is, however, one special set of ortho-normal functions $\chi_k(\epsilon)$ having the special coefficients η_k such that all off-diagonal coefficients η_{ij} are equal to zero, i.e.

$$\Psi(\epsilon_1, \epsilon_2) = \sum_k \eta_k \chi_k(\epsilon_1) \chi_k(\epsilon_2) \quad (2.1)$$

with the condition

$$1 = \sum_k \eta_k^2 \quad (2.2)$$

which insures that the wave function is normalized to unity. The function $\chi_k(\epsilon)$ is called the k-th natural orbital¹³⁻¹⁹ (NO) and the coefficient η_k the k-th natural occupation amplitude. For some properties of the NO's, see Appendix I.

The exact wave function, eq. (2.1), consists of an infinity of configurations and involves an infinity of NO's and natural occupation amplitudes. An approximate N-configuration SCF wave function $\Psi_N(\epsilon_1, \epsilon_2)$ will be defined as that N-configuration wave function which, when written in NO form, consists of the N orbitals $\chi_{N,k}(\epsilon)$ and the N occupation amplitudes $\eta_{N,k}$, $1 \leq k \leq N$, i.e.

$$\Psi_N(\epsilon_1, \epsilon_2) = \sum_{k=1}^N \eta_{N,k} \chi_{N,k}(\epsilon_1) \chi_{N,k}(\epsilon_2). \quad (2.3)$$

The orbitals $\chi_{N,k}(\epsilon)$ will be called the (ground-state) basic N-orbitals and the numbers $\eta_{N,k}$ the N-occupation amplitudes. Equations for the basic N-orbitals and the N-occupation amplitudes can be obtained in

the following manner. Consider the functional $\mathcal{F}_N \{f_1, \dots, f_N\}$,

where

$$\mathcal{F}_N \{f_1, \dots, f_N\} = \frac{2 \sum_{i=1}^N \mu_i^2 \langle f_i | h | f_i \rangle + \frac{1}{Z} \sum_{i,j=1}^N \mu_i \mu_j \langle f_i f_i | \frac{1}{r_{12}} | f_j f_j \rangle}{\sum_{i=1}^N \mu_i^2} \quad (2.4)$$

which is just the expectation value of the Hamiltonian with respect to an arbitrary normalized, two-electron, N-configuration function

$\Phi_N(x_1, x_2)$ written in natural form as

$$\Phi_N(x_1, x_2) = \frac{\sum_{i=1}^N \mu_i f_i(x_1) f_i(x_2)}{\left(\sum_{i=1}^N \mu_i^2 \right)^{1/2}} \quad (2.5)$$

with the constraint

$$\langle f_i | f_j \rangle = \delta_{ij}. \quad (2.6)$$

Those functions for which the functional attains its lowest stationary value subject to the constraints of eq. (2.6) are the basic N-orbitals

$\chi_{N,k}(x)$ which satisfy the following N coupled, non-linear integro-differential equations, $1 \leq k \leq N$,

$$\begin{aligned} & \left[\mu_k h(x_1) + \frac{\mu_k}{Z} \langle X_{N,k} | \frac{1}{r_{12}} | X_{N,k} \rangle - \lambda_{N,kk} \right] X_{N,k}^{(x_1)} \\ & + \sum_{\substack{j=1 \\ j \neq k}}^N \left[\frac{\mu_j}{Z} \langle X_{N,k} | \frac{1}{r_{12}} | X_{N,j} \rangle - \lambda_{N,kj} \right] X_{N,j}^{(x_1)} = 0. \end{aligned} \quad (2.7)$$

Each basic N-orbital is thus a function of the N parameters μ_k . The lowest stationary value of the functional $\mathcal{E}_N\{f_1, \dots, f_N\}$ will be denoted by $\mathcal{E}_N(\mu_1, \dots, \mu_N)$, where

$$\mathcal{E}_N(\mu_1, \dots, \mu_N) = \frac{2 \sum_{i=1}^N \mu_i^2 \langle X_{\mu,i} | h | X_{\mu,i} \rangle + \frac{1}{2} \sum_{i,j=1}^N \mu_i \mu_j \langle X_{\mu,i} X_{\mu,i} | \frac{1}{r_{12}} | X_{\mu,j} X_{\mu,j} \rangle}{\sum_{i=1}^N \mu_i^2} \quad (2.8)$$

which is a function of the N parameters μ_k . The N-occupation amplitudes $\eta_{N,k}$ are obtained by requiring the function $\mathcal{E}_N(\mu_1, \dots, \mu_N)$ to be stationary with respect to variations in the parameters μ_k . That collection of μ_k for which $\mathcal{E}_N(\mu_1, \dots, \mu_N)$ attains its lowest stationary value is the collection of the N-occupation amplitudes which are given by the equations, $1 \leq k \leq N$,

$$\mu_k = \frac{-\frac{1}{2} \sum_{\substack{j=1 \\ j \neq k}}^N \mu_j \langle X_{\mu,k} X_{\mu,k} | \frac{1}{r_{12}} | X_{\mu,j} X_{\mu,j} \rangle}{2 \langle X_{\mu,k} | h | X_{\mu,k} \rangle - \mathcal{E} + \frac{1}{2} \langle X_{\mu,k} X_{\mu,k} | \frac{1}{r_{12}} | X_{\mu,k} X_{\mu,k} \rangle} \quad (2.9)$$

The N-configuration SCF energy E_N is the lowest stationary value of the function $\mathcal{E}_N(\mu_1, \dots, \mu_N)$, i.e.

$$E_N = \mathcal{E}_N(\eta_{N,1}, \dots, \eta_{N,N}). \quad (2.10)$$

The integrals appearing in eqs. (2.7) are

$$\langle X_{\mu,k} | \frac{1}{r_{12}} | X_{\mu,j} \rangle = \int d\tau_2 X_{\mu,k}(\tau_2) \frac{1}{r_{12}} X_{\mu,j}(\tau_2) \quad (2.11)$$

and the quantities $\lambda_{\mu,kj}$ are Lagrange parameters brought in by the ortho-normality constraints, eq. (2.6). They are

$$\lambda_{\mu,kj} = \mu_j \left[\mathcal{E}_N \delta_{kj} - \langle X_{\mu,k} | h | X_{\mu,j} \rangle \right]. \quad (2.12)$$

It will be assumed that the basic N-orbitals have been arranged in some definite order.

In specifying a SCF wave function one must not only specify the number of configurations it is to contain, but one must also specify the angular symmetry of the orbitals out of which the configurations are to be constructed. Therefore, the subscript N on the SCF wave functions and energies must be understood as a list of numbers $(N_0, N_1, \dots, N_L, \dots)$ for $L \geq 0$. The number N_L tells how many L-type configurations the SCF function $\Psi_N(\tau_1, \tau_2)$ contains and thys how many L-type orbitals are involved. (An L-type orbital is an orbital whose angular dependence can be described by an L-th order spherical harmonic.) For two lists M and N, one has that $M > N$ if at least one $M_L > N_L$. The orbitals $\chi_{M,k}^{(L)}$ will be enumerated by writing $1 \leq k \leq M$ or equivalently by writing $1 \leq k \leq N$ and $N + 1 \leq k \leq M$ for $N < M$.

The exact wave function is such that the list defining it has all N_L equal to infinity. The formalism for the NO's can be obtained from the basic N-orbital formalism above by setting all N_L equal to infinity. Thus, in discussing the basic N-orbitals one can also be

discussing the NO's. It will be assumed in the following discussion that all SCF wave functions $\Psi_N(k_1, k_2)$ are constructed to have the correct symmetry properties.

The basic N-orbitals, the parameters μ_k and thus the N-occupation amplitudes can be divided into two sets: the intrinsic orbitals, parameters and occupation amplitudes and the correlation orbitals, parameters and occupation amplitudes. The difference between the two sets can be made clear in the following way. The electronic interaction potential $1/r_{12}$ is always multiplied by the factor $1/Z$ which can be considered as measuring the strength of the electronic interaction relative to the effect of the central field. As $1/Z$ approaches zero the electronic interaction disappears, and each SCF wave function (including the exact wave function) approaches the zero-order wave function discussed at the beginning of Section I, eq. (1.3). The intrinsic N-orbitals are those orbitals which approach the hydrogenic orbitals occurring in the zero-order wave function as $1/Z$ goes to zero. The intrinsic parameters μ_k (and thus the intrinsic N-occupation amplitudes) are those parameters which approach non-zero values as $1/Z$ goes to zero. All other basic N-orbitals, parameters and N-occupation amplitudes are correlation orbitals, parameters and amplitudes. All correlation parameters μ_k approach zero as $1/Z$ approaches zero.

Consider two sets of basic orbitals, e.g. $X_{M,j}^{(k)}$ and $X_{N,k}^{(k)}$ where $1 \leq j \leq M$, $1 \leq k \leq N$ and $N < M$. The first N of the M-orbitals is different from the N-orbitals because the M-orbitals satisfy M coupled equations and the N-orbitals satisfy N coupled equations,

eq. (2.7). However, even though the M-orbitals and N-orbitals are different functions, they are quite similar. If one sets all but the first N parameters μ_k , $1 \leq k \leq N$, in the basic M-orbitals equal to zero, the resulting functions can be divided into two sets. The first N of the resulting functions satisfy the N coupled equations which can be obtained from the first N of the M coupled equations, (eq. (2.7) with M written instead of N) defining the basic M-orbitals by setting all but the first N parameters equal to zero. However, these N coupled equations are just the equations defining the basic N-orbitals, eq. (2.7). The last M-N of the resulting functions will be denoted by $\bar{\chi}_{N,a}^{(k)}$ and satisfy the equations, $a \geq N+1$

$$\bar{\lambda}_{N,aa} \bar{\chi}_{N,a}^{(k)} + \sum_{k=1}^N \left[\frac{\mu_k}{2} \langle \bar{\chi}_{N,a} | \frac{1}{r_{12}} | \chi_{N,k} \rangle - \bar{\lambda}_{N,ak} \right] \chi_{N,k}^{(k)} = 0 \quad (2.13)$$

which have been obtained from the last M-N equations, eq. (2.7), by setting the appropriate parameters equal to zero. The Lagrange parameters $\bar{\lambda}_{N,aa}$ and $\bar{\lambda}_{N,ak}$ have been obtained from the last M-N Lagrange parameters of eq. (2.12) by setting all but the first N parameters μ_k equal to zero. The orbitals $\bar{\chi}_{N,a}^{(k)}$ will be called the complimentary N-orbitals and the Lagrange parameters mentioned above the complimentary Lagrange parameters.

The k-th basic N-orbital and the k-th basic M-orbital satisfy equations having roughly the same form. In fact, every basic orbital satisfies the same type of equation. Every complimentary orbital satisfies the same type of equation which, however, is different from

the type of equation satisfied by the basic orbitals. The equation satisfied by each complimentary N-orbital, eq. (2.13), is not a coupled equation. Each complimentary orbital is required only to be orthogonal to all of the basic N-orbitals. Since the solutions of eq. (2.13) do not in any way depend on the range of the running subscript a , it is artificial to prescribe an upper limit to it. One might as well consider all possible complimentary N-orbitals of which there will be an infinity. It can be readily verified that the complimentary N-orbitals are mutually orthogonal.

In the above discussion the lists M and N were arbitrary except that $M > N$. Therefore the basic N-orbitals can be obtained from any set of basic M orbitals which can thus be obtained from the NO's by setting all but the first M parameters μ_k equal to zero. Therefore, the basic N-orbitals are special cases of the first N NO's, and the complimentary N-orbitals are special cases of the rest of the NO's.

The basic and complimentary N-orbitals $X_{N,k}^{(k)}$ and $\bar{X}_{N,a}^{(k)}$, the Lagrange parameters $\lambda_{N,jk}$ and the function $E_N(\mu_1, \dots, \mu_N)$ are all functions of the N parameters μ_k . Since the parameters μ_j , $j \neq k$, occur in a similar way in eq. (2.7) they probably occur in a similar way in the above-mentioned quantities. However, the parameter μ_k is special. It occurs in eq. (2.7) in a special way, and the above-mentioned quantities depend on it in a unique way. Consider, for example, the k -th NO $X_k^{(k)}$. In setting various parameters μ_j equal to zero, the resulting orbitals are all basic orbitals as long as the k -th parameter μ_k is not equal to zero. As soon as μ_k is set equal to zero, even if it were the

only parameter set equal to zero, the orbital becomes a complimentary orbital. In setting parameters equal to zero one can, of course, never set any of the intrinsic parameters equal to zero.

Consider the list N for which all N_L are equal to zero except N_0 which is equal to unity. Such a list is the (ground-state) RHF list and defines the RHF wave function. The DODS list is such that all N_L are equal to zero except N_0 which is equal to 2, and the EHF list is such that all N_L for $L \geq 1$ are equal to 1 and N_0 is equal to 2. For a physical interpretation of the generalized SCF schemes, see Appendix II.

Since the basic N -orbitals can be considered as special cases of the basic M -orbitals which can be considered as special cases of the NO 's, one can consider the SCF wave function $\Psi_N(\kappa_1, \kappa_2)$ as a special case of the SCF wave function $\Psi_M(\kappa_1, \kappa_2)$ which can be considered as special case of the exact wave function $\Psi(\kappa_1, \kappa_2)$. One must, therefore, have the following relationship

$$E_N \geq E_M \geq E \quad (2.14)$$

where E is the exact energy.

The SCF equations, eq. (2.7), are a complicated set of equations. As will be shown in later sections, they can be solved approximately by perturbation theory. In the following section a convenient perturbation method will be developed and subsequently used to obtain some zero-order basic EHF correlation orbitals.

III. PERTURBATION THEORY

In this section the perturbation expansion based on considering the electronic interaction term in the Hamiltonian as a perturbation will be defined for the two-electron atomic ions in the ground state. The first-order equations will be derived and discussed.

In dealing with the ground state of a two-electron atomic ion, it is convenient to write the problem in terms of the coordinates^{20a} $(r_1, \theta_1, \phi_1, r_2, \theta_{12}, \phi_{12})$ where r_1 , θ_1 and ϕ_1 are the spherical polar coordinates of Electron 1, r_2 is the radial coordinate of Electron 2, and θ_{12} and ϕ_{12} are defined such that

$$\cos \theta_{12} = \cos \theta_1 \cos \theta_2 + \sin \theta_1 \sin \theta_2 \cos(\phi_1 - \phi_2) \quad (3.1)$$

and

$$\sin \phi_{12} \sin \theta_{12} = \sin(\phi_2 - \phi_1) \sin \theta_2. \quad (3.2)$$

In terms of these coordinates the wave function $\Psi(k_1, k_2)$ depends on only r_1 , r_2 and θ_{12} and can be written as

$$\Psi(k_1, k_2) = \frac{1}{\pi \sqrt{8}} \Psi(r_1, r_2, \theta_{12}). \quad (3.3)$$

Therefore, in the following discussion the coordinates θ_1 , ϕ_1 and ϕ_{12} will be neglected. The Schrödinger equation for any S-function can be written as^{20a}

$$\left[-\frac{1}{2r_1} \frac{\partial^2(r_1)}{\partial r_1^2} - \frac{1}{r_1} - \frac{1}{2r_2} \frac{\partial^2(r_2)}{\partial r_2^2} - \frac{1}{r_2} - \frac{1}{2} \left(\frac{1}{r_1^2} + \frac{1}{r_2^2} \right) \frac{1}{\sin \theta_{12}} \frac{\partial}{\partial \theta_{12}} (\sin \theta_{12}) + \frac{1}{2} \cdot \frac{1}{r_{12}} - E \right] \Psi(r_1, r_2, \theta_{12}) = 0. \quad (3.4)$$

It will be assumed that the wave function is normalized to unity. The electronic interaction potential is, in terms of the new coordinates,

$$\frac{1}{r_{12}} = \frac{1}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos \theta_{12}}} \quad (3.5)$$

and can be written as²¹

$$\frac{1}{r_{12}} = \sum_{L=0}^{\infty} \frac{r_{<}^L}{r_{>}^{L+1}} P_L(\cos \theta_{12}) \quad (3.6)$$

where the $P_L(\cos \theta_{12})$ are Legendre polynomials, and $r_{<}$ and $r_{>}$ are the lesser and greater of r_1 and r_2 , respectively. The wave function can be written in the form

$$\Psi(r_1, r_2, \theta_{12}) = \sum_{L=0}^{\infty} \Phi_L(r_1, r_2) \left(\frac{2L+1}{2} \right)^{\frac{1}{2}} P_L(\cos \theta_{12}) \quad (3.7)$$

where $\Phi_0(r_1, r_2)$ will be called the S-component of the wave function and $\Phi_L(r_1, r_2)$ the L-component.

The exact wave function $\Psi(r_1, r_2, \theta_{12})$ is the solution of a rather complicated eigenvalue problem, eq. (3.4), and cannot be obtained in closed form. However, one can obtain a considerable amount of information about $\Psi(r_1, r_2, \theta_{12})$ from a perturbation solution of

eq. (3.4). Even though the perturbation equations cannot be solved in closed form, they are much less complicated than eq. (3.4). The perturbation method of solution is based on considering the electronic interaction potential $1/r_{12}$ as the perturbation. The term $1/Z$ multiplying the $1/r_{12}$ in the Hamiltonian measures the strength of the electronic interaction relative to the central field. Therefore, the natural perturbation expansion parameter is $1/Z$, and the wave function and energy are to be expanded as

$$\Psi(r_1, r_2, \theta_{12}) = \sum_{n=0}^{\infty} \left(\frac{1}{Z}\right)^n \Psi^{(n)}(r_1, r_2, \theta_{12}) \quad (3.8)$$

and

$$E = \sum_{n=0}^{\infty} \left(\frac{1}{Z}\right)^n E^{(n)} \quad (3.9)$$

with the following definitions to fulfill the normalization condition of eq. (2.2):

$$\langle \Psi^{(0)} | \Psi^{(0)} \rangle = 1 \quad (3.10a)$$

and

$$\langle \Psi^{(0)} | \Psi^{(n)} \rangle = 0. \quad (3.10b)$$

Such a perturbation method of solving eq. (3.4) was first used by Hylleraas.^{20b} Even though $1/r_{12}$ is by no means a small quantity, the use of $1/Z$ as an expansion parameter is justified. The wave function and energy expansions, eq. (3.8) and (3.9), are analytic functions of $1/Z$. Knight and Scherr²² assert that the energy expansion converges

absolutely for all $Z > 0.77914$.

The zero-order problem is obtained by neglecting the perturbation $1/r_{12}$ entirely. Therefore, by definition, the zero-order wave function is just the wave function discussed at the beginning of Section I. The zero-order equations are thus the hydrogenic eigenvalue equations for the hydrogenic orbitals from which the zero-order wave function is constructed. The zero-order wave function, eq. (1.3), can be rewritten as

$$\Psi^{(0)}(r_1, r_2, \theta_{12}) = 1S(r_1)1S(r_2) \frac{P_0(\cos\theta_{12})}{\sqrt{2}} \quad (3.11)$$

and also as

$$\Psi^{(0)}(r_1, r_2, \theta_{12}) = \Psi_{L=0}^{(0)}(r_1, r_2) \frac{P_0(\cos\theta_{12})}{\sqrt{2}} \quad (3.12)$$

with all other zero-order L-component functions equal to zero for $L \geq 1$. The zero-order energy (which is not the energy of the zero-order wave function discussed in Section I) $E^{(0)}$ is

$$E^{(0)} = -1.0 \quad \text{a.u.} \quad (3.13)$$

The hydrogenic 1s orbital appearing in the zero-order wave function is just the zero-order intrinsic orbital of the ground state.

The first-order wave function is

$$\Psi^{(1)}(r_1, r_2, \theta_{12}) = \sum_{L=0}^{\infty} \Psi_L^{(1)}(r_1, r_2) \left(\frac{2L+1}{2}\right)^{\frac{1}{2}} P_L(\cos\theta_{12}) \quad (3.14)$$

where

$$\langle \Phi_0^{(0)} | \Phi_0^{(1)} \rangle = 0 \quad (3.15)$$

to satisfy eq. (3.10b). The other first-order component functions need not be orthogonal to the zero-order S-component since the angular functions take care of the orthogonality. Substituting eqs. (3.6), (3.8) and (3.9) into eq. (3.4), equating to zero the coefficient of $1/2$, using eq. (3.14) and extracting out the coefficient of $P_L(\cos\theta_{12})$ by integrating over angles gives the following set of uncoupled first-order differential equations:

$$\begin{aligned} & \left[h_L(r_1) + h_L(r_2) - E^{(0)} \right] \Phi_L^{(1)}(r_1, r_2) + \\ & + \left[\frac{1}{\sqrt{2L+1}} \left(\frac{r_L^L}{r_1^{L+1}} \right) - \delta_{L,0} E^{(1)} \right] \Phi_0^{(0)}(r_1, r_2) = 0 \end{aligned} \quad (3.16)$$

where

$$h_L(r) = -\frac{1}{2r} \frac{\partial^2(r)}{\partial r^2} - \frac{1}{r} + \frac{L(L+1)}{2r^2}. \quad (3.17)$$

The first-order energy $E^{(1)}$ is

$$E^{(1)} = \langle \Phi_0^{(0)} | \frac{1}{r} | \Phi_0^{(0)} \rangle \quad (3.18)$$

and is equal to

$$E^{(1)} = +\frac{5}{8} \text{ a.u.} \quad (3.19)$$

The energy of the zero-order wave function discussed in Section I is equal to the sum of $E^{(0)}$ and $E^{(1)}$. The symbol $\delta_{L,0}$ in eq. (3.16)

is the Kronecker delta.

From the second-order equations, which will not be written down, the following well-known expressions²³ for the second-order energy can be derived:

$$E^{(2)} = \sum_{L=0}^{\infty} E_L^{(2)} \quad (3.20)$$

where

$$E_L^{(2)} = \frac{1}{\sqrt{2L+1}} \left\langle \Phi_L^{(1)} \left| \frac{r_2^L}{r_2^{L+1}} \right| \Phi_0^{(0)} \right\rangle \quad (3.21)$$

or

$$E_L^{(2)} = \left\langle \Phi_L^{(1)}(r_1, r_2) \left| h_L(r_1) + h_L(r_2) - E^{(0)} \right| \Phi_L^{(1)}(r_1, r_2) \right\rangle \\ + \frac{1}{\sqrt{2L+1}} \left\langle \Phi_L^{(1)}(r_1, r_2) \left| \frac{r_2^L}{r_2^{L+1}} \right| \Phi_0^{(0)}(r_1, r_2) \right\rangle \quad (3.22)$$

It is convenient to write the first-order wave function as a sum of two terms: the single-excitation part and the double-excitation part. These excitations are not physical processes and must be understood in the following way. In zero-order, each electron ignores the presence of the other electron and assumes a spatial distribution characteristic of a hydrogenic atom. In first-order the motion of each electron is influenced by the presence of the other electron. Therefore, the spatial distribution of each electron is altered from the zero-order distribution. The alteration of an electron's distribution can be pictured as taking place by allowing it to undergo virtual excitations from the zero-order orbital. These excitations are the single excitations since the other electron always

remains in its zero-order orbital. However, the detailed motions of the electrons are not independent but are correlated. Therefore, there must be a further readjustment of each electron's spatial distribution by means of some cooperative mechanism involving both electrons. This cooperative mechanism can be described by allowing both electrons to undergo virtual excitations from the zero-order orbitals. These excitations are the double excitations for which neither of the electrons remains in the zero-order orbital.

Formally speaking, the first-order wave function must be written as a superposition of an infinite number of configurations. Let $\phi_i(r)$ be the complete set of radial hydrogenic s-orbitals with $\phi_1(r)$ the 1s hydrogenic orbital. The S-component of the first-order wave function can be written as

$$\psi_0^{(1)}(r_1, r_2) = \sum_{i,j}^* c_{ij}^{(1)} \phi_i(r_1) \phi_j(r_2) \quad (3.23)$$

where the asterisk restricts the coefficients such that the zero-order configuration does not appear in the sum. The expansion can be separated into two parts:

$$\psi_0^{(1)}(r_1, r_2) = \psi_{0,SE}^{(1)}(r_1, r_2) + \psi_{0,OE}^{(1)}(r_1, r_2) \quad (3.24)$$

where the single-excitation part of the first-order S-component has the form

$$\psi_{0,SE}^{(1)}(r_1, r_2) = 1s(r_1) F_{(r_2)}^{(1)} + F_{(r_1)}^{(1)} 1s(r_2). \quad (3.25)$$

The function $F_{(r)}^{(1)}$ has the form

$$F^{(1)}(r) = \sum_{j=2}^{\infty} c_{1j}^{(1)} \phi_j(r) \quad (3.26)$$

such that

$$\langle 1s | F^{(1)} \rangle = 0. \quad (3.27)$$

The double-excitation part of the first-order S-component is

$$\Psi_{0,DE}^{(1)}(r_1, r_2) = \sum_{i,j=2}^{\infty} c_{ij}^{(1)} \phi_i(r_1) \phi_j(r_2) \quad (3.28)$$

and is strongly orthogonal to the zero-order orbital, i.e.

$$\langle 1s(r_1) | \Psi_{0,DE}^{(1)}(r_1, r_2) \rangle_{r_1} = \langle 1s(r_2) | \Psi_{0,DE}^{(1)}(r_1, r_2) \rangle_{r_2} = 0 \quad (3.29)$$

where the r_1 outside the brackets indicates integration over that variable. The first-order L-components for $L \geq 1$ are all automatically double-excitation functions since they do not contain the zero-order orbital. Thus, all of the single excitations are condensed into the S-component. The wave function $\Psi(r_1, r_2)$ can likewise be analyzed into single and double excitations. The discussion, however, will be restricted to the first-order problem.

The equations for the single-excitation function $F^{(1)}(r)$ can be obtained from the first-order equation for the S-component, eq. (3.16) with L set equal to zero. Substituting into eq. (3.16) the zero-order wave function from eq. (1.3), the decomposition of the first-order function from eq. (3.24), the form of the single-excitation part of the first-order wave function from eq. (3.25), multiplying by the zero-order orbital and integrating over its coordinates one obtains with the

aid of eq. (3.29) the following equation:

$$\begin{aligned} & \left[h_0(r_1) + \frac{1}{2} \right] F_{(r_1)}^{(1)} \\ & + \left[\langle 1s(r_2) | \frac{1}{r_2} | 1s(r_2) \rangle_{r_2} - E^{(1)} \right] 1s(r_2) = 0 \end{aligned} \quad (3.30)$$

where $E^{(1)}$ has been given by eqs. (3.18) and (3.19). The above equation is identical to the first-order RHF equation^{9a,9b} which gives

$$F_{(r)}^{(1)} = 2e^{-r} \left[\begin{aligned} & \frac{3}{8} [E_i(-2r) - \ln 2r - \gamma] \\ & - \frac{3}{16} \left[\frac{e^{-2r} - 1}{r} \right] - \frac{1}{4} e^{-2r} \\ & + \frac{5}{8} r - \frac{23}{32} + \frac{3}{8} \ln 2 \end{aligned} \right] \quad (3.31)$$

where γ is Euler's constant equal to 0.5772156649 and where $E_i(-2r)$ is the exponential integral defined as $-\int_{-2r}^{\infty} ds \frac{e^{-s}}{s}$.

The equations for the first-order double-excitation functions can be obtained from eqs. (3.16). For the cases $L \geq 1$, eq. (3.16) is the desired equation since all L-component functions for $L \geq 1$ are double-excitation functions. For the case of $L = 0$, the single-excitation part of the S-component function must be first removed. This is accomplished by substituting into eq. (3.16) (with L set equal to zero) the decomposition of the first-order S-component from eq. (3.24) and the form of the single-excitation part of the S-component from eq. (3.25). Using eq. (3.30) to simplify the result, one obtains the desired equation. Thus, for $L \geq 0$,

$$\begin{aligned} & \left[h_L(r_1) + h_L(r_2) - E^{(0)} \right] \Phi_{L,DE}^{(1)}(r_1, r_2) \\ & + \frac{1}{\sqrt{2L+1}} Q_L(r_1, r_2) \left(\frac{r_2^L}{r_2^{L+1}} \right) \Phi_0^{(0)}(r_1, r_2) = 0 \end{aligned} \quad (3.32)$$

where $Q_L(r_1, r_2)$ is the following projection operator

$$Q_L(r_1, r_2) = 1 - |1s(r_1)\rangle \delta_{L,0} \langle 1s(r_1)| \\ - |1s(r_2)\rangle \delta_{L,0} \langle 1s(r_2)| \\ + |1s(r_1) 1s(r_2)\rangle \delta_{L,0} \langle 1s(r_1) 1s(r_2)| \quad (3.33)$$

which guarantees that the solution of the double-excitation S-type equation is strongly orthogonal to the zero-order orbital. The second-order energy can be separated into the single-excitation and double-excitation contributions. One has

$$E_L^{(2)} = E_{L,SE}^{(2)} \delta_{L,0} + E_{L,DE}^{(2)} \quad (3.34)$$

where

$$E_{0,SE}^{(2)} = \langle \psi_{0,SE}^{(1)} | \frac{1}{r} | \psi_0^{(0)} \rangle \quad (3.35)$$

and

$$E_{L,DE}^{(2)} = \frac{1}{\sqrt{2L+1}} \langle \psi_{L,DE}^{(1)} | \frac{r_L^L}{r^{L+1}} | \psi_0^{(0)} \rangle \quad (3.36)$$

or

$$E_{L,DE}^{(2)} = \langle \psi_{L,DE}^{(1)}(r_1, r_2) | h_L(r_1) + h_L(r_2) - E | \psi_{L,DE}^{(1)}(r_1, r_2) \rangle \\ + \frac{2}{\sqrt{2L+1}} \langle \psi_{L,DE}^{(1)}(r_1, r_2) | \frac{r_L^L}{r^{L+1}} | \psi_0^{(0)}(r_1, r_2) \rangle \quad (3.37)$$

The separation of the first-order problem into a single-excitation part and a double-excitation part has been easily accomplished. The second- and higher-order perturbation equations do not separate

quite so neatly, but they do separate. This separation is akin to the usual separation of the wave function into the RHF part and the correlation part.^{24,25} Even though the single-excitation function is not the RHF function and the correlation function is not the double-excitation function, they are identical through first-order in $1/Z$. Both the single-excitation function and the RHF wave function serve to adjust the spatial distribution of each electron to the average field of the other electron. This adjustment takes place one electron at a time. Thus, the first-order single-excitation or RHF equation, eq. (3.30), adjusts the spatial distribution of Electron 1 to the average field of Electron 2. The average field of Electron 2, $\langle \psi(r_2) | \frac{1}{r_1} | \psi(r_2) \rangle_{r_2}$, is computed with the zero-order orbital which is previously known. The second-order distribution of Electron 1 would in the same way adjust itself to the average field of Electron 2 which is calculated with only the previously known zero-order and first-order orbitals.

The details of the electronic motion, to first-order, are contained in the first-order double-excitation function which is identical to the first-order correlation function. In the next section the distinction between the single-excitation processes and the double-excitation processes will become clear. It will turn out that each correlation or double-excitation NO satisfies an integro-differential equation which shows how the two electrons must simultaneously adjust their charge distributions to each other.

IV. PERTURBATION EXPANSION OF THE SELF-CONSISTENT FIELD EQUATIONS FOR THE TWO-ELECTRON ATOMIC IONS

The perturbation method developed in the previous section will be applied to the general N-configuration SCF schemes discussed in Section II. The procedure to be used will be to transform the exact first-order formalism of the previous section into NO form and then to obtain the first-order formalism for any N-configuration SCF scheme by setting equal to zero the appropriate parameters.

Since the ground-state wave function can be written as a sum of L-component functions, eq. (3.7), the NO's can be split into sets according to angular symmetry. Since the first-order equation can be separated into different equations for each angular component, the NO equation can likewise be separated into sets of equations for each L-type NO. The parameters μ_k and the natural occupation amplitudes η_k will be thus labeled μ_{Lk} and η_{Lk} . Since the first-order equations are radial equations, only the radial parts of the NO's need be considered. They will be labeled as $\chi_{Lk}^{(r)}$, and the angular dependence will not be considered. The L-component of the wave function will be written as

$$\Phi_L(r_1, r_2) = \sum_{k=1}^{\infty} \eta_{Lk} \chi_{Lk}^{(r_1)} \chi_{Lk}^{(r_2)} \quad (4.1)$$

where

$$\langle \chi_{Lj} | \chi_{Lk} \rangle = \delta_{jk}. \quad (4.2)$$

Natural orbitals belonging to different component functions do not have any special overlap properties. The normalization condition

for the exact wave function, eq. (2.2), is

$$1 = \sum_{L=0}^{\infty} \sum_{k=1}^{\infty} \eta_{Lk}^2. \quad (4.3)$$

To effect a perturbation expansion of the NO equations one must expand the NO's, the parameters μ_{Lk} and the natural occupation amplitudes η_{Lk} in powers of $1/Z$ as

$$\chi_{Lk}^{(n)} = \sum_{n=0}^{\infty} \left(\frac{1}{Z}\right)^n \chi_{Lk}^{(n)}, \quad (4.4)$$

$$\mu_{Lk} = \sum_{n=0}^{\infty} \left(\frac{1}{Z}\right)^n \mu_{Lk}^{(n)} \quad (4.5a)$$

and

$$\eta_{Lk} = \sum_{n=0}^{\infty} \left(\frac{1}{Z}\right)^n \eta_{Lk}^{(n)}. \quad (4.5b)$$

The zero-order L-component function written in NO form is, from eq. (4.1),

$$\Psi_L^{(0)}(r_1, r_2) = \sum_{k=1}^{\infty} \eta_{Lk}^{(0)} \chi_{Lk}^{(0)}(r_1) \chi_{Lk}^{(0)}(r_2) \quad (4.6)$$

and written in terms of the hydrogenic orbitals is

$$\Psi_L^{(0)}(r_1, r_2) = \delta_{L,0} 1s(r_1) 1s(r_2). \quad (4.7)$$

Comparing the two forms leads one to the conclusion that

$$\eta_{Lk}^{(0)} = \begin{cases} 1; & L=0, k=1 \\ 0; & \text{otherwise} \end{cases} \quad (4.8a)$$

and

$$\chi_{07}^{(0)}(r) = 1s(r). \quad (4.8b)$$

The first-order S-component written in NO form is

$$\begin{aligned} \mathcal{G}_0^{(1)}(r_1, r_2) = & \chi_{07}^{(0)}(r_1) \chi_{07}^{(1)}(r_2) + \chi_{07}^{(1)}(r_1) \chi_{07}^{(0)}(r_2) \\ & + \eta_{07}^{(1)} \chi_{07}^{(0)}(r_1) \chi_{07}^{(0)}(r_2) \\ & + \sum_{k=2}^{\infty} \eta_{0k}^{(1)} \chi_{0k}^{(0)}(r_1) \chi_{0k}^{(0)}(r_2) \end{aligned} \quad (4.9)$$

and written in terms of hydrogenic and single-excitation orbitals is

$$\mathcal{G}_0^{(1)}(r_1, r_2) = 1s(r_1) F(r_2) + F(r_1) 1s(r_2). \quad (4.10)$$

Comparing these two forms yields, keeping in mind eq. (3.29),

$$\eta_{0k}^{(1)} = \begin{cases} 0; & k=1 \\ \text{non-zero;} & \text{otherwise} \end{cases} \quad (4.11a)$$

and

$$\chi_{07}^{(1)}(r) = F(r). \quad (4.11b)$$

There is only one intrinsic NO and one intrinsic natural occupation amplitude for the ground state. They are $\chi_{07}^{(0)}$ and η_{07} respectively, and as far as zero order and first order go are defined independently of the correlation NO's and correlation natural occupation amplitudes. The zero-order and first-order intrinsic NO and intrinsic amplitude are common to all first-order SCF wave

functions. (The second- and higher-order-intrinsic NO's and intrinsic natural occupation amplitudes depend on the double-excitation part of the wave function.) Therefore, the following discussion will be concerned only with the correlation NO's. As far as the intrinsic NO's and the entire single-excitation problem is concerned, the NO formalism does not offer any particular advantages.

The real advantage of the NO form manifests itself in treating the double excitations. From the first-order part of eq. (4.1) (neglecting the single-excitation part) one has that

$$\psi_{L,OE}^{(0)}(r_1, r_2) = \sum_{k=k_L}^{\infty} \eta_{Lk}^{(1)} X_{Lk}^{(0)}(r_1) X_{Lk}^{(0)}(r_2) \quad (4.12)$$

where k_L is equal to 1 for $L \geq 1$ and equal to 2 for $L = 0$. One has, from eq. (4.2),

$$\langle X_{Lj}^{(0)} | X_{Lk}^{(0)} \rangle = \delta_{jk} \quad (4.13)$$

for all NO's, $j, k \geq 1$. The equation for the correlation orbital $X_{Lk}^{(0)}(r)$ is obtained by substituting eq. (4.12) into eq. (3.32), multiplying by $X_{Lk}^{(0)}(r_2)$ and integrating over r_2 . Thus, for $L \geq 0$ and for $k \geq k_L$,

$$\begin{aligned} & \left[u_{Lk}^{(1)} h_L(r) + V_L(r) - \lambda_{Lk}^{(1)} \right] X_{Lk}^{(0)}(r) \\ & - \sum_{\substack{j=k_L \\ j \neq k}}^{\infty} \lambda_{Lkj}^{(1)} X_{Lj}^{(0)}(r) = 0 \end{aligned} \quad (4.14)$$

where the first-order Lagrange parameters are

$$\lambda_{Lk}^{(1)} = \mu_{Lj}^{(1)} \left[E^{(0)} \delta_{kj} - \langle x_{Lk}^{(0)} | h_L | x_{Lk}^{(0)} \rangle \right] \quad (4.15)$$

and the average interaction potential $V_L(r_1)$ is

$$V_L(r_1) = \frac{1}{\sqrt{2L+1}} \langle 1s(r_2) | q_L(r_1) \times \left(\frac{r_2^L}{r_2^{L+1}} \right) P(1,2) | 1s(r_2) \rangle_{r_2} \quad (4.16)$$

The r_2 outside the brackets indicates integration over r_2 , and

$P(1,2)$ is a permutation operator which interchanges r_1 and r_2 in the functions following it prior to integration. The quantity $q_L(r_1)$ is the following projection operator

$$q_L(r_1) = 1 - |1s(r_1)\rangle \delta_{L,0} \langle 1s(r_1)| \quad (4.17)$$

which insures that all s-type NO's are orthogonal to the zero-order intrinsic orbital.

The infinite set of coupled equations (4.14) for the zero-order correlation NO's can be obtained by requiring the functional

$\tilde{\mathcal{F}}_L^{(2)} \{f_{Lk}, \dots\}$, where

$$\tilde{\mathcal{F}}_L^{(2)} \{f_{Lk}, \dots\} = \sum_{k=k_L}^{\infty} \tilde{\mathcal{F}}_{Lk}^{(2)} \{f_{Lk}\} \quad (4.18)$$

with

$$\begin{aligned} \tilde{\mathcal{F}}_{Lk}^{(2)} \{f_{Lk}\} = & 2 (\mu_{Lk}^{(1)})^2 \langle f_{Lk} | h_L | f_{Lk} \rangle \\ & - (\mu_{Lk}^{(1)})^2 E^{(0)} \\ & + 2 \mu_{Lk}^{(1)} \langle f_{Lk} | V_L | f_{Lk} \rangle, \end{aligned} \quad (4.19)$$

to be stationary with respect to variations in all of the $f_{Lk}(r)$ subject to the constraints

$$\langle f_{Lk} | f_{Lj} \rangle = \delta_{kj} \quad (4.20)$$

for $L \geq 0$, $j, k \geq k_L$. The lowest stationary value of $\mathcal{E}_L^{(2)} \{f_{Lk}, \dots\}$ will be denoted by $\mathcal{E}_L^{(2)}(\mu_{Lk_L}^{(1)}, \dots)$ and occurs when each $f_{Lk}(r)$ is equal to the zero-order k -th NO $X_{Lk}^{(0)}$, $k \geq k_L$. Since each NO is a function of the infinity of parameters $\mu_{Lk}^{(1)}$, $k \geq k_L$, so is the quantity $\mathcal{E}_L^{(2)}(\mu_{Lk_L}^{(1)}, \dots)$ which can be written as

$$\mathcal{E}_L^{(2)}(\mu_{Lk_L}^{(1)}, \dots) = \sum_{k=k_L}^{\infty} \mathcal{E}_{Lk}^{(2)}(\mu_{Lk_L}^{(1)}, \dots) \quad (4.21)$$

where

$$\begin{aligned} \mathcal{E}_{Lk}^{(2)}(\mu_{Lk_L}^{(1)}, \dots) = & 2(\mu_{Lk}^{(1)})^2 \langle X_{Lk}^{(0)} | h_L | X_{Lk}^{(0)} \rangle \\ & - (\mu_{Lk}^{(1)})^2 E^{(0)} \\ & + 2\mu_{Lk}^{(1)} \langle X_{Lk}^{(0)} | V_L | X_{Lk}^{(0)} \rangle \end{aligned} \quad (4.22)$$

The L -component of the double-excitation part of the second-order energy, $E_{L,DE}^{(2)}$, is obtained by requiring $\mathcal{E}_L^{(2)}(\mu_{Lk_L}^{(1)}, \dots)$ to be stationary with respect to variations in the parameters $\mu_{Lk}^{(1)}$. The set of first-order natural occupation amplitudes $\eta_{Lk}^{(1)}$ is that set of values of the $\mu_{Lk}^{(1)}$ for which $\mathcal{E}_L^{(2)}(\mu_{Lk_L}^{(1)}, \dots)$ attains its lowest stationary value, i.e.

$$E_{L,DE}^{(2)} = \mathcal{E}_L^{(2)}(\eta_{Lk_L}^{(1)}, \dots). \quad (4.23)$$

It is to be emphasized that the stationary point for $E_L^{(2)}(\mu_{Lk}^{(1)}, \dots)$ is not a stationary point for any of the $E_{Lk}^{(2)}(\mu_{Lk}^{(1)}, \dots)$, eq. (4.22).

One thus has

$$E_{L,DE}^{(2)} = \sum_{k=h_L}^{\infty} E_{Lk}^{(2)} \quad (4.24)$$

where

$$E_{Lk}^{(2)} = \eta_{Lk}^{(1)} \langle X_{Lk}^{(0)} | V_L | X_{Lk}^{(0)} \rangle \quad (4.25)$$

with

$$\eta_{Lk}^{(1)} = \frac{-\langle X_{Lk}^{(0)} | V_L | X_{Lk}^{(0)} \rangle}{2 \langle X_{Lk}^{(0)} | H_L | X_{Lk}^{(0)} \rangle - E^{(0)}} \quad (4.26)$$

which is obtained by requiring

$$\frac{\partial E_L^{(2)}(\mu_{Lk}^{(1)}, \dots)}{\partial \mu_{Lk}^{(1)}} = 0. \quad (4.27)$$

It is shown in Appendix III that

$$\eta_{Lk}^{(1)} \leq 0 \quad (4.28)$$

for all L and all $k \geq 1$. Therefore, from eq. (4.25) all of the $E_{Lk}^{(2)}$ must be negative and thus, from eq. (4.24), all second-order energies must be negative, i.e.

$$E_{L,DE}^{(2)} \leq 0. \quad (4.29)$$

All of the diagonal Lagrange parameters $\lambda_{Lk}^{(1)}$ evaluated at the stationary point must be positive since in general, from eqs. (4.14) and (4.22),

$$\epsilon_{Lk}^{(2)} = 2\mu_{Lk}^{(1)} \lambda_{Lkk}^{(1)} - (\mu_{Lk}^{(1)})^2 E^{(0)} \quad (4.30)$$

From eq. (4.14) one can see that the case for which all the $\mu_{Lk}^{(1)}$ are negative corresponds to the potential $V_L(r)$ being attractive. Thus, positive values of the diagonal Lagrange parameters correspond to bound-state solutions of eq. (4.14) and to negative second-order energies. The lowest energy solution of eq. (4.14) is $X_{Lk_L}^{(0)}$ and is associated with the highest positive $\lambda_{Lkk}^{(1)}$.

The perturbation formalism for the N-configuration SCF schemes can be obtained from the NO formalism by setting all but the first N parameters $\mu_{Lk}^{(1)}$ equal to zero. The zero-order formalism for any N-configuration SCF scheme must be identical with the exact zero-order formalism. The first-order RHF formalism is just the single-excitation formalism of the previous section written in terms of the zero- and first-order intrinsic orbitals. The single-excitation part of the first-order formalism for any SCF scheme is identical to the first-order RHF formalism and involves only the intrinsic basic orbital.

To separate once and for all the single-excitation part out of the first-order formalism of any N-configuration SCF scheme for the ground state one can proceed as follows. For all possible N-configuration wave functions $\Phi_{L_N}^{(1)}(\kappa_1, \kappa_2)$ one has, for the ground state,

$$\Phi_{L_N}^{(1)}(\kappa_1, \kappa_2) = \frac{1}{\pi\sqrt{8}} \Phi_{L_N}^{(1)}(\kappa_1, \kappa_2, \theta_{12}) \quad (4.31)$$

where

$$\Psi_L^{(1)}(r_1, r_2, \theta_{12}) = \sum_{L=0}^{\infty} \Psi_{N,L}^{(1)}(r_1, r_2) \left(\frac{2L+1}{2}\right)^{\frac{1}{2}} P_L(\cos\theta_{12}). \quad (4.32)$$

The S-component of every first-order SCF function can be divided into the single-excitation and double-excitation parts, i.e.

$$\Psi_{N,0}^{(1)}(r_1, r_2) = \Psi_{N,0,SE}^{(1)}(r_1, r_2) + \Psi_{N,0,DE}^{(1)}(r_1, r_2) \quad (4.33)$$

where

$$\Psi_{N,0,SE}^{(1)}(r_1, r_2) = 7s(r_1) F^{(1)}(r_2) + F^{(1)}(r_1) 7s(r_2). \quad (4.34)$$

The double-excitation functions are thus, for $L \geq 0$,

$$\Psi_{N,L,DE}^{(1)}(r_1, r_2) = \sum_{k=k_L}^{\infty} \gamma_{N,L,k}^{(1)} X_{N,L,k}^{(0)}(r_1) X_{N,L,k}^{(0)}(r_2) \quad (4.35)$$

where the sum includes just the zero-order correlation basic orbitals.

The intrinsic basic N-orbital $X_{N,0}^{(0)}$ is, to zero order,

$$X_{N,0}^{(0)}(r) = 2e^{-r} \quad (4.36a)$$

and, to first order, (see eq. (3.31)),

$$X_{N,0}^{(1)}(r) = 2e^{-r} \left[\begin{aligned} &\frac{3}{8} [E_i(-2r) - \frac{1}{4} 2r - \gamma] \\ &- \frac{3}{16} \left[\frac{e^{-2r} - 1}{r} \right] - \frac{1}{4} e^{-2r} \\ &+ \frac{5}{8} r - \frac{23}{32} + \frac{3}{8} \ln 2 \end{aligned} \right] \quad (4.36b)$$

The intrinsic N-occupation amplitude is, to zero order,

$$\eta_{N,01}^{(0)} = 1 \quad (4.37a)$$

and, to first-order,

$$\eta_{N,01}^{(1)} = 0. \quad (4.37b)$$

The single-excitation contribution to any SCF second-order energy^{9a} is, for all SCF schemes,

$$E_{N,0,SE}^{(2)} = -\frac{13}{864} + \frac{9}{64} \ln\left(\frac{3}{4}\right) \text{ a.u.} \quad (4.38a)$$

or

$$E_{N,0,SE}^{(2)} = -0.111\,003\,18 \text{ a.u.} \quad (4.38b)$$

Setting all but the first N parameters $\mu_{Lk}^{(1)}$ equal to zero splits the infinite set of equations, eq. (4.14), into two sets:

the finite set for the basic correlation N-orbitals $X_{N,Lk}^{(0)}$,

$$k_L \leq k \leq N_L, L \geq 0,$$

$$\left[\mu_{Lk}^{(1)} h_L(r_1) + V_L(r_1) - \lambda_{N,Lk}^{(1)} \right] X_{N,Lk}^{(0)} - \sum_{\substack{j=k_L \\ j \neq k}}^{N_L} \lambda_{N,Lk}^{(1)} X_{N,Lj}^{(0)} = 0 \quad (4.39)$$

and the infinite set for the complimentary N-orbitals $\bar{X}_{N,La}^{(0)}$,

$$a \geq N_L + 1,$$

$$[V_L(\epsilon) - \bar{\lambda}_{N,Laa}^{(1)}] \bar{X}_{N,La}^{(0)} + \sum_{j=k_L}^{N_L} \bar{\lambda}_{N,Laj}^{(1)} X_{N,Lj}^{(0)} = 0 \quad (4.40)$$

where, from eq. (4.13),

$$\langle X_{N,Lk}^{(0)} | X_{N,Lj}^{(0)} \rangle = \delta_{kj}, \quad (4.41a)$$

$$\langle \bar{X}_{N,La}^{(0)} | \bar{X}_{N,Lb}^{(0)} \rangle = \delta_{ab} \quad (4.41b)$$

and

$$\langle \bar{X}_{N,La}^{(0)} | X_{N,Lk}^{(0)} \rangle = 0. \quad (4.41c)$$

From eq. (4.15), one has

$$\lambda_{N,Lkj}^{(1)} = \mu_{Lj}^{(1)} \left[E^{(0)} \delta_{kj} - \langle X_{N,Lk}^{(0)} | h_L | X_{N,Lj}^{(0)} \rangle \right] \quad (4.42a)$$

or

$$\begin{aligned} \lambda_{N,Lkj}^{(1)} = \mu_{Lk}^{(1)} & \langle X_{N,Lk}^{(0)} | h_L | X_{N,Lj}^{(0)} \rangle \\ & + \langle X_{N,Lk}^{(0)} | V_L | X_{N,Lj}^{(0)} \rangle \end{aligned} \quad (4.42b)$$

and also

$$\bar{\lambda}_{N,Laa}^{(1)} = \langle \bar{X}_{N,La}^{(0)} | V_L | \bar{X}_{N,La}^{(0)} \rangle \quad (4.43)$$

and

$$\bar{\lambda}_{N,L,k}^{(1)} = -\mu_{L,k}^{(1)} \langle \bar{X}_{N,L,a}^{(0)} | h_L | \bar{X}_{N,L,k}^{(0)} \rangle \quad (4.44a)$$

or

$$\bar{\lambda}_{N,L,k}^{(1)} = \langle \bar{X}_{N,L,a}^{(0)} | V_L | X_{N,L,k}^{(0)} \rangle. \quad (4.44b)$$

Similarly to the case of the NO's, the equations (4.39) for the zero-order basic N-orbitals $X_{N,L,k}^{(0)}$, $k_L \leq k \leq N_L$, can be obtained by requiring the functional $\tilde{F}_{N,L}^{(2)} \{f_{L,k_L}, \dots, f_{L,N_L}\}$, where

$$\tilde{F}_{N,L}^{(2)} \{f_{L,k_L}, \dots, f_{L,N_L}\} = \sum_{k=k_L}^{N_L} \tilde{F}_{L,k}^{(2)} \{f_{L,k}\} \quad (4.45)$$

with the $\tilde{F}_{L,k}^{(2)} \{f_{L,k}\}$ given by eq. (4.19), to be stationary with respect to variations in all of the $f_{L,k}$ subject to the constraints given by eq. (4.20). The lowest stationary value of the functional is attained when each $f_{L,k}$ is equal to $X_{N,L,k}^{(0)}$ and will be denoted by $\mathcal{E}_{N,L}^{(2)}(\mu_{L,k_L}^{(1)}, \dots, \mu_{L,N_L}^{(1)})$, where

$$\mathcal{E}_{N,L}^{(2)}(\mu_{L,k_L}^{(1)}, \dots, \mu_{L,N_L}^{(1)}) = \sum_{k=k_L}^{N_L} \mathcal{E}_{N,L,k}^{(2)}(\mu_{L,k_L}^{(1)}, \dots, \mu_{L,N_L}^{(1)}) \quad (4.46)$$

with

$$\begin{aligned} \mathcal{E}_{N,L}^{(2)}(\mu_{L,k_L}^{(1)}, \dots, \mu_{L,N_L}^{(1)}) &= 2(\mu_{L,k}^{(1)})^2 \langle X_{N,L,k}^{(0)} | h_L | X_{N,L,k}^{(0)} \rangle \\ &\quad - (\mu_{L,k}^{(1)})^2 E^{(0)} \\ &\quad + 2 \mu_{L,k}^{(1)} \langle X_{N,L,k}^{(0)} | V_L | X_{N,L,k}^{(0)} \rangle \end{aligned} \quad (4.47)$$

which is a function of the parameters $\mu_{Lk}^{(1)}$, $k_L \leq k \leq N_L$.

The L-component of the double-excitation part of the second-order N-configuration SCF energy, $E_{N,L,DE}^{(2)}$ is obtained by requiring the function $\mathcal{E}_{N,L}^{(2)}$ to be stationary with respect to variations in the parameters $\mu_{Lk}^{(1)}$. There may be many sets of values for these parameters which lead to stationary values for $\mathcal{E}_{N,L}^{(2)}$, but the required set is that one which leads to the lowest stationary value. Thus,

$$E_{N,L,DE}^{(2)} = \sum_{k=k_L}^{N_L} E_{N,Lk}^{(2)} \quad (4.48)$$

where

$$E_{N,Lk}^{(2)} = \eta_{N,Lk}^{(1)} \langle X_{N,Lk}^{(0)} | V_L | X_{N,Lk}^{(0)} \rangle \quad (4.49)$$

with

$$\eta_{N,Lk}^{(1)} = \frac{-\langle X_{N,Lk}^{(0)} | V_L | X_{N,Lk}^{(0)} \rangle}{2\langle X_{N,Lk}^{(0)} | H_L | X_{N,Lk}^{(0)} \rangle - E^{(0)}} \quad (4.50)$$

which are the special values of the parameters obtained by requiring

$$\frac{\partial \mathcal{E}_{N,L}^{(2)}}{\partial \mu_{Lk}^{(1)}} = 0. \quad (4.51)$$

Just as the quantities $\mathcal{E}_{Lk}^{(2)}$, the $\mathcal{E}_{N,Lk}^{(2)}$ are not stationary for those values of the parameters which make $\mathcal{E}_{N,L}^{(2)}$ stationary.

Similarly to the NO's, one has that

$$\eta_{N,Lk}^{(1)} \leq 0 \quad (4.52)$$

and

$$E_{N,L,DE}^{(2)} \leq 0 \quad (4.53)$$

since all $E_{N,L,k}^{(2)}$ are negative. All diagonal Lagrange parameters evaluated at the stationary point are positive since, in general,

$$\mathcal{E}_{N,L,k}^{(2)} = 2\mu_{N,L,k}^{(1)} \lambda_{N,L,k}^{(1)} - (\mu_{N,L,k}^{(1)})^2 E^{(0)} \quad (4.54)$$

The equations for all zero-order complimentary N-orbitals $\bar{X}_{N,L,a}^{(0)}$ can be obtained from the functional $\bar{\mathcal{F}}_L^{(2)}\{f\}$, where

$$\bar{\mathcal{F}}_L^{(2)}\{f\} = \langle f | V_L | f \rangle \quad (4.55)$$

by requiring it to be stationary with respect to variations in the function f subject to the constraints

$$\langle f | f \rangle = 1 \quad (4.56a)$$

and

$$\langle f | X_{N,L,k}^{(0)} \rangle = 0 \quad (4.56b)$$

for $k_L \leq k \leq N_L$. The values of the function $\mathcal{E}_{N,L}^{(2)}$ are zero for all complimentary orbitals.

All of the zero-order correlation basic and complimentary N-orbitals are functions of the parameters $\mu_{L,k}^{(1)}$. This dependence will be discussed in the next section in connection with the first-order EHF scheme.

V. THE ZERO-ORDER EXTENDED HARTREE-FOCK ORBITALS

The EHF scheme is such a SCF scheme whose wave function consists of two s-type orbital configurations and one L-type orbital configuration for each $L \geq 1$. The EHF scheme involves one correlation basic orbital of each angular type and is thus the simplest SCF scheme which takes all types of angular correlation into account. The DODS wave function consists of two s-orbital configurations, which are, through first order in $1/Z$, identical with the EHF s-orbital configurations. The DODS wave function is the simplest radial function which takes radial correlation into account. Thus, in discussing the first-order s-type EHF equations one is also discussing the first-order DODS equations. In this section the first-order EHF equations¹² for the ground state will be discussed, and the relationship of the zero-order EHF orbitals to the zero-order NO's will be investigated.

The single-excitation part of the first-order EHF problem can be factored out and the intrinsic orbital and occupation amplitude disposed of as in the previous section, eqs. (4.31) to (4.38b). The formalism for the zero-order correlation EHF orbitals can be obtained from eqs. (4.39) to (4.56b) by writing "EHF" in place of "N" and by limiting the ranges of all indices to the one value k_L .

The one basic correlation EHF orbital of each angular type is just the first correlation NO of each angular type with all correlation parameters $M_{Lk}^{(n)}$ except the first one set equal to zero. The complimentary EHF orbitals are all the other NO's with all but the

first correlation parameter set equal to zero. Suppose, however, that all correlation parameters except the k -th one were set equal to zero. In such a case the k -th NO would become an "excited" basic EHF orbital while all other NO's would be turned into complimentary EHF orbitals. Therefore, one can have many different EHF orbitals and thus as many different sets of complimentary EHF orbitals. In Section II it was always assumed that all but the lowest few correlation parameters were set equal to zero in obtaining basic orbitals from NO's. Excited basic orbitals such as the excited EHF orbitals mentioned above were not considered in Section II.

The zero-order basic correlation EHF orbitals will be denoted by $X_{EHF,Lk}^{(0)}$ and the first-order EHF occupation amplitudes by $\gamma_{EHF,Lk}^{(1)}$ $k \geq k_L$. The set of zero-order EHF orbitals complimentary to the basic EHF orbital $X_{EHF,Lk}^{(0)}$ will be denoted $\bar{X}_{EHF,Lk,a}^{(0)}$, $a \neq k$. The equations for the zero-order basic EHF orbitals are, from eq. (4.39),

$$\left[\mu_{Lk}^{(1)} h_L(\epsilon_k) + V_L(\epsilon_k) - \lambda_{EHF,Lk}^{(1)} \right] X_{EHF,Lk}^{(0)} = 0 \quad (5.1)$$

with no upper limit on the index k . The equations for the zero-order complimentary EHF orbitals, from eq. (4.40), are

$$\begin{aligned} \left[V_L(\epsilon_k) - \bar{\lambda}_{EHF,Lk,a}^{(1)} \right] \bar{X}_{EHF,Lk,a}^{(0)} &= \\ &= \bar{\lambda}_{EHF,Lk,a}^{(1)} X_{EHF,Lk}^{(0)} \end{aligned} \quad (5.2)$$

where the only restriction on the index a is $a \neq k$. The definitions of the Lagrange parameters appearing in the above equations are

given by eqs. (4.41a) to (4.44b) of Section IV.

It should be noted that the equations for the zero-order EHF orbitals are all uncoupled, i.e. each basic orbital satisfies an equation independent of all the other basic EHF orbitals. This is to be expected since there is really only one correlation EHF orbital - the lowest energy solution of eq. (5.1) (i.e. the solution associated with the highest positive $\lambda_{EHF,LK}^{(1)}$). All solutions of eq. (5.1), the lowest one and the excited ones, are tied to the ground state by the form of the potentials $V_L(r_1)$, eq. (4.16). In view of the connection of the EHF orbitals with the NO's, one can consider the parameters $\mu_{LK}^{(1)}$ as different entities or alternatively, as different values of one and the same thing.

Since the basic and complimentary N-orbitals are special cases of the NO's, one would expect the general characteristics of any N-configuration SCF scheme to be the same as those of the NO scheme. In other words, one would expect that the functional form of the k-th N-orbital and the relative magnitudes of two Lagrange parameters $\lambda_{N,kj}$ and two functions $\mathcal{E}_{N,k}$ to be the same as for the NO's. This supposition can be made plausible for the zero-order EHF orbitals in the following manner.

Consider eq. (5.1), and let it be rewritten in the form

$$\left[\mathcal{H}_L(r_1; \mu_{LK}^{(1)}) - \lambda_{EHF,LK}^{(1)} \right] X_{EHF,LK}^{(0)} = 0 \quad (5.3)$$

where

$$\mathcal{H}_L(r_1; \mu_{LK}^{(1)}) = \mu_{LK}^{(1)} h_L(r_1) + V_L(r_1). \quad (5.4)$$

For a fixed value of the parameter $\mu_{Lk}^{(1)}$ the operator \mathcal{H}_L is Hermitian with respect to all suitably integrable functions. (The functions must be orthogonal to the 1s hydrogenic orbital if L is equal to zero.) Equation (5.3) is therefore, for a fixed value of the parameter, an eigenvalue equation with $\lambda_{EHF,Lk}^{(1)}$ as eigenvalues and the $X_{EHF,Lk}^{(0)}$ as eigenfunctions. The eigenvalues will all be real and, for negative values of the parameter, will be positive. The eigenfunctions will be mutually orthogonal only for equal values of the parameters $\mu_{Lk}^{(1)}$ and $\mu_{Lj}^{(1)}$, since, from eq. (5.1),

$$\begin{aligned} & (\lambda_{EHF,Lk}^{(1)} - \lambda_{EHF,Lj}^{(1)}) \langle X_{EHF,Lk}^{(0)} | X_{EHF,Lj}^{(0)} \rangle = \\ & = (\mu_{Lk}^{(1)} - \mu_{Lj}^{(1)}) \langle X_{EHF,Lk}^{(0)} | h_L | X_{EHF,Lj}^{(0)} \rangle. \end{aligned} \quad (5.5)$$

Each of $X_{EHF,Lk}^{(0)}$, $\lambda_{EHF,Lk}^{(1)}$ and $\mathcal{E}_{EHF,Lk}^{(2)}$ is a function of only the one parameter $\mu_{Lk}^{(1)}$. In the limit as the parameter approaches zero, the eigenvalue equation, eq. (5.3), approaches the equation

$$\left[V_L(r) - \lambda_{EHF,Lk}^{(1)} \right] X_{EHF,Lk}^{(0)} = 0 \quad (5.6)$$

where the limiting orbitals and Lagrange parameters have been designated as $X_{EHF,Lk}^{(0)}$ and $\lambda_{EHF,Lk}^{(1)}$, respectively. From eq. (4.47), the limiting values of the $\mathcal{E}_{EHF,Lk}^{(2)}$ are zero for all k.

The limiting orbitals are just the zero-order complimentary RHF orbitals $\bar{X}_{RHF,Lk}^{(0)}$. Writing

$$\alpha_{Lk}^2 = \frac{4}{\sqrt{2L+1}} \frac{1}{\lambda_{EHF, Lk}^{(1)}(0)} \quad (5.7)$$

and

$$X_{EHF, Lk}^{(1)}(r; 0) = \frac{e^{-r}}{r} G_{Lk}(r) \quad (5.8)$$

and differentiating eq. (5.6) twice with respect to r_1 gives the equation

$$\frac{d^2 G_{Lk}(r)}{dr^2} + \alpha_{Lk}^2 e^{-2r} G_{Lk}(r) - \frac{L(L+1)}{2r^2} G_{Lk}(r) = 0 \quad (5.9)$$

which can be solved for $L=0$ to give, $k \geq k_L$,

$$X_{EHF, 0k}^{(1)}(r; 0) = N_{0k} \frac{e^{-r}}{r} \left[Y_0(\alpha_{0k} e^{-r}) - \frac{2}{\pi} \left(\ln \frac{\alpha_{0k}}{2} + \gamma \right) J_0(\alpha_{0k} e^{-r}) \right] \quad (5.10)$$

where α_{0k} is the k -th largest solution of the equation

$$\frac{Y_0(\alpha_{0k})}{J_0(\alpha_{0k})} = \frac{2}{\pi} \left(\ln \frac{\alpha_{0k}}{2} + \gamma \right) \quad (5.11)$$

and must thus be positive. The functions J_0 and Y_0 are the ordinary Bessel functions²⁶ of order zero of the first and second kinds, respectively, N_{0k} is a normalization constant and γ is Euler's constant. The orbitals $X_{EHF, 0k}^{(1)}(r; 0)$ have all been constructed to be orthogonal to the $1s$ hydrogenic orbital although the solutions of eq. (5.9) need not be so. The k -th orbital has $k-1$ nodes. If the orbitals are arranged according to increasing number of nodes,

$X_{EHF,0j}^{(0)}$, having fewer nodes than $X_{EHF,0k}^{(0)}$ if $j < k$, then one would have, from eq. (5.7), that $\lambda_{EHF,0jj}^{(1)} > \lambda_{EHF,0kk}^{(1)}$.

Although the solutions of eq. (5.9) could not be obtained for $L \geq 1$, one supposes that would have the same kinds of properties as the ones discussed for the case $L=0$ above.

In the case that the parameter $\mu_{LR}^{(1)}$ approaches negative infinity, all of the diagonal Lagrange parameters $\lambda_{EHF,Lk}^{(1)}$ approach positive infinity. However, the quantities $\epsilon_{EHF,Lk}^{(1)}$ defined as

$$\epsilon_{EHF,Lk}^{(1)} = \frac{\lambda_{EHF,Lk}^{(1)}}{\mu_{LR}^{(1)}} \quad (5.12)$$

remain finite for $\mu_{LR}^{(1)}$ non-zero. The limiting orbitals and limiting epsilons will be denoted $X_{EHF,Lk}^{(10)}$ and $\epsilon_{EHF,Lk}^{(10)}$ for $\mu_{LR}^{(1)}$ equal to negative infinity. Equation (5.3) thus becomes the limiting equation

$$\left[h_L(r) - \epsilon_{EHF,Lk}^{(10)} \right] X_{EHF,Lk}^{(10)} = 0 \quad (5.13)$$

for $k \geq k_L$ and is just the equation for the hydrogenic orbitals.

If $\phi_{LR}(r)$ denotes the k -th hydrogenic orbital of L -th angular type, one has that

$$X_{EHF,Lk}^{(10)} = \phi_{LR}(r) \quad (5.14a)$$

and

$$\epsilon_{EHF,Lk}^{(10)} = -\frac{1}{2} \frac{1}{(L+k)^2}. \quad (5.14b)$$

Therefore the limiting function $X_{EHF,Lk}^{(0)}(r;\infty)$ has k nodes for $L \geq 1$ and $k-1$ nodes for $L = 0$. If the orbitals are arranged according to

increasing number of nodes, one then has the relationship

$|E_{EHF,L}^{(1)}| > |E_{EHF,Lk}^{(1)}|$ where the bars indicate absolute value. This ordering of the epsilons is in the same direction as the ordering of the $\lambda_{EHF,0kk}^{(1)}$

The structure of the eigenvalue problem, eq. (5.3), is the same for $\mu_{Lk}^{(1)}$ equal to zero and to negative infinity. (Since for positive values of the parameters $\mu_{Lk}^{(1)}$ the second-order energies are positive and the Lagrange parameters $\lambda_{EHF,Lk}^{(1)}$ are negative, eq. (5.3) approaches the hydrogenic equation with positive and thus continuous eigenvalues in the limit that $\mu_{Lk}^{(1)}$ approaches positive infinity.) The number of solutions does not depend on the particular value given to $\mu_{Lk}^{(1)}$ nor does the nodal structure of the solutions or the ordering of the eigenvalues. Both limiting forms of the orbitals, $X_{EHF,Lk}^{(0)}(r;0)$ and $X_{EHF,Lk}^{(0)}(r;\infty)$, behave like hydrogenic functions near zero which is just how the orbitals $X_{EHF,Lk}^{(0)}$ must behave. By writing out the solutions of eqs. (5.1) and (5.9) one can show that for any value of $\mu_{Lk}^{(1)}$

$$\lim_{r \rightarrow 0} \left(\frac{X_{EHF,Lk}^{(0)}(r;\infty)}{r^L} \right) = \text{const.} \quad (5.15)$$

Therefore, it seems reasonable to assume that the structure of the eigenvalue problem, eq. (5.3), is independent of the parameters $\mu_{Lk}^{(1)}$.

The above discussions lends some plausibility to considering the k -th EHF orbital as just the k -th NO with all but the k -th

parameter $\mu_{Lk}^{(1)}$ set equal to zero, and similarly for the Lagrange parameters $\lambda_{EHF,Lk}^{(1)}$, the functions $\mathcal{E}_{EHF,Lk}^{(2)}$ and the energies $\mathcal{E}_{EHF,Lk}^{(2)}$. One can thus consider the function $X_{EHF,Lk}^{(10)}(r, \infty)$, eq. (5.14a), as the k-th NO with all parameters set equal to zero except $\mu_{Lk}^{(1)}$ which is equal to negative infinity. Since these limiting orbitals (together with the 1s hydrogenic orbital) form a complete set of one-electron functions, one would suspect that the zero-order intrinsic and correlation NO's formed a complete set of one-electron functions. This is a reasonable conclusion since the operator $\mathcal{H}_L(r, \mu_{Lk}^{(1)})$ eq. (5.4), is a Hermitian operator. One would also suspect that the exact NO's $X_{Lk}^{(10)}$ discussed in Section II form a complete set of one-electron functions.

The limiting functions $X_{EHF,Lk}^{(10)}(r, 0)$, eq. (5.10), can be considered as special cases of the NO's and therefore, (together with the 1s hydrogenic orbital) as forming a complete set of one-electron functions. However, since eq. (5.6) can be rewritten as

$$\frac{1}{\sqrt{2}} X_{EHF,Lk}^{(10)}(r_1, 0) = \left\langle \left(\frac{r_2^L}{r_2^{L+1}} e^{-\eta} e^{-\eta_2} \right) \middle| X_{EHF,Lk}^{(10)}(r_2, 0) \right\rangle_{r_2} \quad (5.16)$$

$$- \mathcal{E}_k \delta_{L,0} 1s(r_1)$$

where

$$\mathcal{E}_k = \left\langle 1s(r_1) 1s(r_2) \middle| \frac{1}{r_1} \middle| 1s(r_1) X_{EHF,Lk}^{(10)}(r_2, 0) \right\rangle, \quad (5.17)$$

the limiting basic orbitals $X_{EHF,Lk}^{(10)}(r, 0)$ (which are also the zero-order complimentary RHF orbitals) are (constrained) natural orbitals

of the functions $\left(\frac{r_L^L}{r_L^{L+1}} e^{-\eta} e^{-\frac{r}{2}}\right)$, $L \geq 0$, with $\frac{1}{\alpha_{Lk}}$ as the natural occupation amplitudes of these functions. In fact, from eqs. (4.40) and (4.55) one can see that any set of complimentary orbitals is a suitably constrained set of natural orbitals of the function $\left(\frac{1}{r_{12}} e^{-\eta} e^{-\frac{r}{2}}\right)$. The unconstrained natural orbitals of this function form a complete set of one-electron functions. Since the natural expansion of $\left(\frac{1}{r_{12}} e^{-\eta} e^{-\frac{r}{2}}\right)$ (and thus of $\frac{1}{r_{12}}$) requires a complete set of functions, one suspects that all the natural occupation amplitudes η_k of the two-electron wave function are non-zero.

The function $\mathcal{E}_{Lk}^{(2)}$, eq. (4.22), is a function of the infinity of parameters $\mu_{Lk}^{(1)}$ which can be considered as coordinates. Thus, each $\mathcal{E}_{Lk}^{(2)}$ can be considered as a surface in an infinite-dimensional coordinate space. Each surface has extreme values at those points whose coordinates $\mu_{Lk}^{(1)}$ satisfy the equations

$$2\mu_{Lk}^{(1)} \langle X_{Lk}^{(0)} | h_L | X_{Lk}^{(0)} \rangle - \mu_{Lk}^{(1)} E^{(0)} + 2 \langle X_{Lk}^{(0)} | V_L | X_{Lk}^{(0)} \rangle \quad (5.18a)$$

$$- 2\mu_{Lk}^{(1)} \sum_{j \neq k} \mu_{Lj}^{(1)} \langle X_{Lk}^{(0)} | h_L | X_{Lj}^{(0)} \rangle \times \left\langle \frac{\partial X_{Lk}^{(0)}}{\partial \mu_{Lk}^{(1)}} | X_{Lj}^{(0)} \right\rangle = 0$$

and, for $i \neq k$,

$$\sum_{j \neq k} \mu_{Lj}^{(1)} \langle X_{Lk}^{(0)} | h_L | X_{Lj}^{(0)} \rangle \left\langle \frac{\partial X_{Lk}^{(0)}}{\partial \mu_{Li}^{(1)}} | X_{Lj}^{(0)} \right\rangle = 0 \quad (5.18b)$$

which were obtained by requiring

$$\frac{\delta \mathcal{E}_{Lk}^{(2)}}{\delta \mu_{Li}^{(1)}} = 0 \quad (5.19)$$

for all $i \geq k_L$. (See eqs. (4.22) and (4.42a).) Each surface $\mathcal{E}_{Lk}^{(2)}$ is zero along each axis in the coordinate space except the $\mu_{Lk}^{(1)}$ -axis. The projection of $\mathcal{E}_{Lk}^{(2)}$ on the $\mu_{Lk}^{(1)}$ -axis is just the function $\mathcal{E}_{EHF,Lk}^{(2)}$, eq. (4.47). At the origin of the coordinate space each surface $\mathcal{E}_{Lk}^{(2)}$ is zero. At the negative infinity end of the $\mu_{Lk}^{(1)}$ -axis it is equal to positive infinity which fact can be deduced from eqs. (4.54), (5.12) and (5.14b). From eqs. (5.18) one knows that there must be at least one stationary or extreme value of the surface $\mathcal{E}_{Lk}^{(2)}$ (or $\mathcal{E}_{EHF,Lk}^{(2)}$) along the $\mu_{Lk}^{(1)}$ -axis. Let the lowest of these stationary values be called $E_{EHF,Lk}^{(2)}$, and let it occur at the point at which $\mu_{Lk}^{(1)}$ has the value $\eta_{EHF,Lk}^{(1)}$. One thus has, from eqs. (4.49) to (4.56), $k \geq k_L$, that

$$E_{EHF,Lk}^{(2)} = \eta_{EHF,Lk}^{(1)} \langle X_{EHF,Lk}^{(0)} | V_L | X_{EHF,Lk}^{(0)} \rangle \quad (5.20)$$

with

$$\eta_{EHF,Lk}^{(1)} = \frac{-\langle X_{EHF,Lk}^{(0)} | V_L | X_{EHF,Lk}^{(0)} \rangle}{2 \langle X_{EHF,Lk}^{(0)} | h_L | X_{EHF,Lk}^{(0)} \rangle - E^{(0)}} \quad (5.21)$$

which can also be obtained from eq. (5.18a). Since all $\eta_{EHF,Lk}^{(1)}$ are negative (see eq. (4.52)), the values $E_{EHF,Lk}^{(2)}$, $k \geq k_L$, must all be negative and must thus correspond to minimum values of the

$\epsilon_{Lk}^{(2)}$ (or $\epsilon_{EHF,Lk}^{(2)}$). The L-component of the double-excitation part of the second-order EHF energy $E_{EHF,L,DE}^{(2)}$ is

$$E_{EHF,L,DE}^{(2)} = E_{EHF,Lk_L}^{(2)}. \quad (5.22)$$

The quantities $E_{EHF,Lk}^{(2)}$, $k \geq k_L + 1$, are the second-order energies associated with the excited EHF orbitals.

There are in general many other stationary values of $\epsilon_{Lk}^{(2)}$ lying off of the $\mu_{Lk}^{(1)}$ -axis since there are in general many solutions of eqs. (5.18). Since the EHF orbital $\chi_{EHF,Lk_L}^{(0)}$ is the lowest solution of eq. (5.1) (has the highest positive $\lambda_{EHF,Lk_L}^{(1)}$) one must have

$$\epsilon_{EHF,Lk_L}^{(2)} \leq \epsilon_{N,Lk_L}^{(2)}. \quad (5.23)$$

This inequality can be demonstrated in the following way. The function $\chi_{N,Lk_L}^{(0)}$ which defines $\epsilon_{N,Lk_L}^{(2)}$, eq. (4.47), can be expanded in the set of solutions of eq. (5.1), i.e.

$$\chi_{N,Lk_L}^{(0)} = \sum_{j=k_L}^{\infty} d_j \chi_{EHF,Lj}^{(0)} \quad (5.24)$$

with

$$1 = \sum_{j=k_L}^{\infty} d_j^2 \quad (5.25)$$

It was mentioned at the beginning of this section that the parameters

$\mu_{Lk}^{(1)}$ could be considered as distinct entities or as different values of one and the same thing. Up to now the parameter $\mu_{Lk}^{(1)}$ has been considered as a different entity from the parameter $\mu_{Lj}^{(1)}$. However, in the following discussion let $\mu_{Lk}^{(1)}$ and $\mu_{Lj}^{(1)}$ be considered as particular values of one and the same parameter $\mu^{(1)}$.

Therefore, eq. (5.1) can be rewritten as

$$\left[\mu^{(1)} h_L(\nu_1) + V_L(\nu_1) - \lambda_{EHF, Lk}^{(1)} \right] X_{EHF, Lk}^{(0)} = 0. \quad (5.26)$$

From eq. (4.47) one has

$$\begin{aligned} \mathcal{E}_{N, Lk_L}^{(2)} = & 2\mu^{(1)} \sum_{i,j=k_L}^{\infty} d_i d_j \langle X_{EHF, Li}^{(0)} | \mu^{(1)} h_L(\nu_1) + \\ & + V_L(\nu_1) | X_{EHF, Lj}^{(0)} \rangle \\ & - (\mu^{(1)})^2 E^{(0)} \end{aligned} \quad (5.27)$$

and from eq. (5.26)

$$\mathcal{E}_{N, Lk_L}^{(2)} = 2\mu^{(1)} \sum_{j=k_L}^{\infty} d_j^2 \lambda_{EHF, Lj}^{(1)} - (\mu^{(1)})^2 E^{(0)} \quad (5.28)$$

Using eqs. (4.54) and (5.25), one has

$$\begin{aligned} \mathcal{E}_{N, Lk_L}^{(2)} - \mathcal{E}_{EHF, Lk_L}^{(2)} = \\ = 2\mu^{(1)} \sum_{j=k_L}^{\infty} d_j^2 \left(\lambda_{EHF, Lj}^{(1)} - \lambda_{EHF, Lk_L}^{(1)} \right) \end{aligned} \quad (5.29)$$

and since $\lambda_{EHF, Lk_L}^{(1)}$ is the highest positive eigenvalue of

eq. (5.26), eq. (5.23) must follow. Unfortunately, one cannot say

anything about the relative magnitudes of $\mathcal{E}_{EHF, Lk}^{(2)}$ and the $\mathcal{E}_{N, Lk}^{(2)}$ for $k > k_L$.

VI. NUMERICAL SOLUTION OF THE FIRST-ORDER EXTENDED HARTREE-FOCK EQUATIONS

Approximate numerical solutions of several first-order EHF equations, eq. (5.1), were obtained. In this section the numerical method will be described and some second-order EHF energies will be tabulated.

Each zero-order EHF basic correlation orbital $\chi_{EHF,LR}^{(0)}, k \geq k_L$, was approximated by the following type of (truncated) expansion in terms of the complete set of functions $f_{Ln}(r)$, i.e.

$$\chi_{EHF,LR}^{(0)} = \sum_n \tilde{C}_{Lk,n} f_{Ln}(r). \quad (6.1)$$

The functions $f_{Ln}(r)$ are the associated Laguerre functions,^{27,28}

$$f_{Ln}(r) = 2^{3/2} \sqrt{\frac{n!}{(2L+n+2)!}} (2r)^L \sum_n \binom{2L+2}{2r} e^{-r} \quad (6.2)$$

$n \geq 0$, and have the convenient feature of possessing no continuum contribution. (The functions $f_{Ln}(r)$ are not exactly those of references 27 and 28; for details see Appendix IV.) Some sample calculations were performed using a scale factor, but since the optimal value of the scale factor turned out to be very close to unity no scale factor was used in the calculations.

Each first-order EHF differential equation, eq. (5.1), was replaced by the finite set of linear equations

$$\sum_n \left(\tilde{M}_{LR}^{(1)} h_{L,mn} + V_{L,mn} - \tilde{\lambda}_{EHF,LR}^{(1)} \delta_{m,n} \right) \tilde{C}_{Lk,n} = 0 \quad (6.3)$$

where the optimal value of $\tilde{\mu}_{LK}^{(1)}$ is given, from eq. (4.50), by

$$\tilde{\mu}_{LK}^{(1)} = \frac{- \sum_{m,n} \tilde{C}_{Lk,m} V_{L,mn} \tilde{C}_{Lk,n}}{1 + 2 \sum_{m,n} \tilde{C}_{Lk,m} h_{L,mn} \tilde{C}_{Lk,n}} \quad (6.4)$$

The quantities $h_{L,mn}$ and $V_{L,mn}$ are matrix elements of the operators h_L and V_L , eqs. (3.17) and (4.16) respectively, with respect to the functions $\tilde{\phi}_{Ln}^{(1)}$. For details, see Appendix IV. The tilde over a quantity indicates a numerical approximation to the quantity.

Since the orbitals $\tilde{\chi}_{EHF,LK}^{(1)}$ are approximate because they are expressed as truncated expansions of a complete set of functions, one can use MacDonald's theorems²⁹ to show that (for negative $\mu_{LK}^{(1)}$)

$$0 \leq \tilde{\lambda}_{EHF,LK}^{(1)} \leq \lambda_{EHF,LK}^{(1)} \quad (6.5)$$

and thus, from eq. (4.54), that

$$0 \geq \tilde{\epsilon}_{EHF,LK}^{(2)} \geq \epsilon_{EHF,LK}^{(2)} \quad (6.6)$$

for any given value of $\tilde{\mu}_{LK}^{(1)}$. However, since the optimal value $\tilde{\eta}_{EHF,LK}^{(1)}$ will in general be different from the value $\eta_{EHF,LK}^{(1)}$ one has that

$$0 \geq \tilde{E}_{EHF,LK}^{(2)} \geq E_{EHF,LK}^{(2)} \quad (6.7)$$

which states that any numerical second-order EHF energy is an upper bound to the true second-order EHF energy. Unfortunately, nothing can be said about the relation between $\tilde{\eta}_{EHF,LK}^{(1)}$ and $\eta_{EHF,LK}^{(2)}$.

The coefficients $\tilde{c}_{LK,n}$ were obtained by solving equations (6.3) and (6.4) interactively.^{1,30} A value of $\tilde{\mu}_{LK}^{(1)}$ was guessed and used in eq. (6.3) which was then solved as an eigenvalue problem. Using the values obtained for the coefficients $\tilde{c}_{LK,n}$ from eq. (6.3), a new value for $\tilde{\mu}_{LK}^{(1)}$ was calculated from eq. (6.4) and was used as the next guess in solving eq. (6.3). This cycle was repeated until the values of $\tilde{\epsilon}_{EHF,LK}^{(2)}$, eq. (4.47), calculated with two successive guesses for $\tilde{\mu}_{LK}^{(1)}$ agreed to a prescribed number of significant figures. When such agreement was attained, the last guess for $\tilde{\mu}_{LK}^{(1)}$ was called $\tilde{\eta}_{EHF,LK}^{(1)}$, and the corresponding value of $\tilde{\epsilon}_{EHF,LK}^{(2)}$ was called $\tilde{\epsilon}_{EHF,LK}^{(12)}$. The EHF energies in atomic units and occupation amplitudes so obtained are listed in Tables I through III. Each result quoted corresponds to a forty term expansion of the function $\chi_{EHF,LK}^{(1)}$. The coefficients $\tilde{c}_{LK,n}$ for the various functions are listed in Appendix V. The calculations were performed on a CDC 1604 computer using a Fortran 63 program. The eigenvalue problem, eq. (6.3), was solved by diagonalizing the secular determinant with a Jacobi rotation method.³¹

Although the first-order EHF equations could not be solved analytically, they were easily programmed with a general program for all angular types. In the next section the perturbation results of Tables I through III will be compared with other values from the

TABLE I

Some Second-Order EHF S-component Energies^a

k	$\gamma_{EHF,0k}^{(1)}$	$E_{EHF,02}^{(2)} \times 10^{-2}$	$E_{EHF,03}^{(2)} \times 10^{-4}$	$E_{EHF,04}^{(2)} \times 10^{-5}$	$E_{EHF,05}^{(2)} \times 10^{-5}$
2	-0.89009×10^{-1}	<u>-1.32060</u>	64.838	722.72	751.06
3	-0.87826×10^{-2}	-0.28896	<u>-4.16507</u>	5.496	6.898
4	-2.2104×10^{-3}	-0.07821	-2.7283	<u>-5.1618</u>	-0.07806
5	-0.81×10^{-4}	-0.0290	-0.911	-3.47	<u>-1.12</u>

a The numbers in bold type are the $E_{EHF,0k}^{(2)}$

TABLE II

Some Second-Order EHF P-component Energies

k	$\eta_{EHF,1k}^{(1)}$	$\mathcal{E}_{EHF,11}^{(2)}$ $\times 10^{-2}$ ~~~~~	$\mathcal{E}_{EHF,12}^{(2)}$ $\times 10^{-3}$	$\mathcal{E}_{EHF,13}^{(2)}$ $\times 10^{-4}$	$\mathcal{E}_{EHF,14}^{(2)}$ $\times 10^{-5}$
1	-1.18200×10^{-1}	-2.35373 ~~~~~	11.07	112.6	1320.2
2	-1.7×10^{-2}	-0.70595	-1.26 ~~~	1.8	240.
3	-4.3×10^{-3}	-0.205	-0.669	-1.73 ~~~	-0.319
4	-1.6×10^{-3}	-0.077	-0.29	-1.17	-3.86 ~~~

TABLE III

Some Second-Order EHF L-component Energies

L	$\gamma_{EHF,L}^{(1)}$	$E_{EHF,L}^{(2)}$
2	-2.7732×10	-3.0391×10^{-3}
3	-1.0226×10^{-2}	-7.3958×10^{-4}
4	-4.74×10^{-3}	-2.482×10^{-4}
5	-2.52×10^{-3}	-1.017×10^{-4}
6	-1.48×10^{-3}	-4.78×10^{-5}
7	-0.94×10^{-3}	-2.48×10^{-5}

literature. The second-order EHF energies $E_{EHF,L}^{(2)}$ seem to depend on the $-1/3$ power of L . This is a much weaker dependence than the L^{-4} dependence predicted by Schwartz³² for the exact second-order energies $E_{L,OE}^{(2)}$.

VII. DISCUSSION OF THE RESULTS

As discussed in Section II there are two types of SCF schemes: The RHF scheme containing only intrinsic orbitals and thus neglecting electron correlation, and the other SCF schemes containing at least one correlation orbital. For the case of the helium atom the difference between the RHF energy and the exact non-relativistic energy is about 0.04 atomic unit and is, by definition, the correlation energy.^{3,24} The variational approximation to the EHF wave function of Silverman, Platas and Matsen⁷ yielded about 0.03 atomic unit of correlation energy. One can thus see that it takes the infinity of SCF schemes lying between the EHF scheme and the exact wave function to yield that last 0.01 atomic unit of correlation energy. Therefore, if one wants an energy much more accurate than the EHF energy, one should probably not use a SCF method to get it.

The accuracy of the EHF scheme has been assessed by comparing, Table IV, several second-order EHF L-component energies with the corresponding exact values. The comparison is the most unfavorable comparison one can make. A more practical comparison is made in Table V in which the EHF energies through second order

$$E_{EHF} \approx -Z^2 + \frac{5}{8} Z + E_{SE}^{(2)} + E_{EHF,OE}^{(2)} \quad (7.1)$$

TABLE IV
Comparison of Several Second-Order EHF
and Exact Energies

L	EHF ^a	Exact ^b	Error %
0	-0.0132060	-0.01432881	8
1	-0.0235373	-0.02644609	11
2	-0.0030391	-0.00361237	16

a See eq. (5.22)

b Taken from Table I of reference 33

TABLE V

Comparison of Some Second-Order Perturbation Results with More Accurate Energies ^a				
	Z=1		Z=2	
	CI ^b	EHF ^c	CI	EHF
RHF	-0.48793	-0.48600	-2.91668	-2.86100
S	-0.51439	-0.49921	-2.87896	-2.87421
S+P	-0.52647	-0.52275	-2.90039	-2.89775
S+P+D	-0.52730	-0.52579	-2.90258	-2.90079
S+...+F	-0.52747	-0.52653	-2.90307	-2.90153
S+...+G	-0.52775	-0.52677	-2.90320	-2.90177
S+...+J		-0.52695		-2.90195
Exact ^d	-0.52775	-0.5272	-2.90372	-2.9021
	Z=3		Z=8	
	CI	EHF	CI	EHF
RHF	-7.23641	-7.23600	-59.11114	-59.11100
S	-7.25242	-7.24921	-59.12595	-59.12421
S+P	-7.27575	-7.27275	-59.15130	-59.14775
S+P+D	-7.27845	-7.27579	-59.15467	-59.15079
S+...+F	-7.27908	-7.27653	-59.15549	-59.15153
S+...+G	-7.27924	-7.27677	-59.15570	-59.15177
S+...+J		-7.27695		-59.15195
Exact	-7.27991	-7.2770	-59.15660	-59.1521

a in atomic units

b Taken from Table II of reference 35

c These values are sums of the $E_{EHF, L_k}^{(2)}$

d The value in the EHF column is an extrapolation of the first seven values.

in atomic units, are compared with several configuration interaction (CI) results. Although the EHF energies through second order are not necessarily upper bounds or lower bounds to the exact energies, they nevertheless compare favorably in Table V with the CI results. The EHF contribution to the second-order correlation energy is about 0.0415 atomic unit as compared to the more accurate value of 0.046652 atomic unit quoted by Sharma and Coulson.³⁴

Various contributions to the second-order EHF double-excitation energies are compared in Table VI with some approximate values obtained from an iterative³⁶ solution of the NO equations (eq. (2.7) with N set to infinity). One thus sees from Table VI that the second-order EHF energies are roughly the same as the other more elaborate correlation contributions. Since the comparison of the second-order EHF energies with iterative solutions of the exact NO equations is quite good, it will be even better with the iterative EHF correlation energies. Therefore, one might as well not solve the unperturbed EHF equations. The second-order energies are good enough.

In conclusion, it might be said that if one wants very good energies he should not use a SCF method. However, if one will be satisfied with the gross effects of electronic correlation, then he could probably use the results of the first-order EHF model quite profitably.

TABLE VI

Comparison of Some Second-Order EHF Energy Contributions
with Some Approximate Correlation Energy Contributions

contrib.	EHF ^a	Z=1	Z=2	Z=3	Z=8
		ΔE_{corr}^b			
2s	-0.01321	-0.01879	-0.01522	-0.01443	-0.01358
3s	-0.00042	-0.00043	-0.00067	-0.00072	-0.00075
4s	-0.00005	-0.00005	-0.00009	-0.00011	-0.00009
5s	-0.00001	-0.00001	-0.000004	-0.000002	-0.000001
2p	-0.02354	-0.01391	-0.01943	-0.02092	-0.02255
3p	-0.00126	-0.00089	-0.00157	-0.00186	-0.00206
4p	-0.00017	-0.00013	-0.00016	-0.00016	-0.00013
5p	-0.00004	-0.00003	-0.000005	-0.000003	-0.000002
3d	-0.00394	-0.00131	-0.00218	-0.00244	-0.00275
4f	-0.00074	-0.00026	-0.00036	-0.00037	-0.00036

a These are the $E_{\text{EHF}, \text{Lk}}^{(2)}$ taken from Tables I, II and III

b Taken from Table IV of reference 36.

APPENDIX I: THE NATURAL ORBITALS OF TWO-ELECTION WAVE FUNCTIONS

The natural orbitals were first introduced by Löwdin¹³ in 1955 as that set of one-electron functions which diagonalizes the one-particle density matrix. The one-particle density matrix,³⁷ $\rho(\underline{x}_1, \underline{x}'_1)$ with \underline{x} being the collection of space and spin variables, which is defined as

$$\rho(\underline{x}_1, \underline{x}'_1) = \int \Psi(\underline{x}_1, \underline{x}_2, \dots, \underline{x}_N) \Psi^*(\underline{x}'_1, \underline{x}_2, \dots, \underline{x}_N) d\underline{x}_2 \dots d\underline{x}_N \quad (\text{I.1})$$

for any N-electron wave function $\Psi(\underline{x}_1, \dots, \underline{x}_N)$ can thus be written as a diagonal expansion

$$\rho(\underline{x}_1, \underline{x}'_1) = \sum_k n_k \chi_k(\underline{x}_1) \chi_k^*(\underline{x}'_1) \quad (\text{I.2})$$

where $\chi_k(\underline{x})$ is the k-th NO and n_k is the k-th occupation number. If the wave function is normalized to unity the sum of the occupation numbers is equal to unity. For the special case in which the wave function is a two-electron wave function, Löwdin and Shull¹⁴ have shown that the wave function can also be written as a diagonal expansion in terms of the NO's with the coefficients γ_k , i.e.

$$\Psi(\underline{x}_1, \underline{x}_2) = \sum_k \gamma_k \chi_k(\underline{x}_1) \chi_k^*(\underline{x}_2) \quad (\text{I.3})$$

where

$$n_k = |\gamma_k|^2 \quad (\text{I.4})$$

The two-electron wave function, expanded in terms of a complete set of suitable functions $\phi_i(x)$ e.g.

$$\Psi(x_1, x_2) = \sum_{ij} c_{ij} \phi_i(x_1) \phi_j(x_2) \quad (1.5)$$

can be brought into natural form by diagonalizing the matrix of coefficients c_{ij} . Shull and Lowdin^{14,15} have obtained several NO's for the helium atom by expanding the two-electron wave function in a finite set of functions (as in eq. (1.5)), determining the coefficients and then diagonalizing the coefficient matrix. Since they used a finite set of basis functions in expanding the two-electron wave function, they obtained only a finite number of approximate NO's.

Davidson^{16,17} in 1962 worked out the formalism for obtaining the NO's from a two-electron wave function explicitly containing the coordinate r_{12} . He pointed out that one can obtain more information about the NO's by defining them in terms of the wave function rather than the density matrix. The following discussion of the NO's associated with a two-electron wave function will be based on Davidson's point of view.

Let $\Psi(x_1, x_2)$ be a real two-electron spatial wave function which is either symmetric or antisymmetric with respect to permutation of the coordinates of the two electrons, i.e.

$$P(1,2) \Psi(x_1, x_2) = \pm \Psi(x_1, x_2) \quad (1.6)$$

where $P(1,2)$ is the permutation operator and σ is equal to +1 for a symmetric function and -1 for an antisymmetric wave function. A natural orbital $\chi(\zeta)$ associated with the wave function $\Psi(\zeta_1, \zeta_2)$ is defined to be that function which extremizes the functional

$$\eta = \int \chi^*(\zeta_1) \Psi(\zeta_1, \zeta_2) \chi(\zeta_2) d\zeta_1 d\zeta_2 \quad (I.7)$$

subject to the normalization constraint

$$1 = \int \chi^*(\zeta) \chi(\zeta) d\zeta. \quad (I.8)$$

As Lowdin and Shull showed,¹⁴ the NO $\chi(\zeta)$ can be considered as that orbital such that the function $\chi(\zeta_1) \chi(\zeta_2)$ has maximum overlap with the exact wave function. Setting the variation of η with respect to arbitrary variations in $\chi(\zeta)$ subject to the constraint of eq. (I.8) equal to zero leads to the integral eigenvalue equation

$$\eta_k \chi_k(\zeta_1) = \int \Psi(\zeta_1, \zeta_2) \chi_k(\zeta_2) d\zeta_2 \quad (I.9)$$

where the NO $\chi_k(\zeta)$ is the eigenfunction associated with the eigenvalue η_k , usually called the k-th occupation amplitude. The above equation will, in general, have many eigenvalues and many eigenfunctions.

The symmetry properties of the wave function can be exploited to obtain some information about the eigenvalues and eigenfunctions. Suppose that η_k is an eigenvalue given by

$$\eta_k = \int X_k^*(\kappa_1) \psi(\kappa_1, \kappa_2) X_k(\kappa_2) d\tau_1 d\tau_2. \quad (I.10)$$

By exchanging the names of the integration variables in the above equation, taking the complex conjugate and permuting the variables in the wave function, one can obtain the expression

$$\sigma \eta_k^* = \int X_k^*(\kappa_1) \psi(\kappa_1, \kappa_2) X_k(\kappa_2) d\tau_1 d\tau_2 \quad (I.11)$$

from which it follows that

$$\eta_k = \sigma \eta_k^*. \quad (I.12)$$

Therefore, if $\psi(\kappa_1, \kappa_2)$ is symmetric, the occupation amplitudes are all real, and if $\psi(\kappa_1, \kappa_2)$ is antisymmetric the occupation amplitudes are all imaginary (or zero). By taking the complex conjugate of eq. (I.9) one can obtain

$$\eta_k^* X_k^*(\kappa_1) = \int \psi(\kappa_1, \kappa_2) X_k^*(\kappa_2) d\tau_2 \quad (I.13)$$

which implies that, if the wave function is symmetric, the NO's are all real functions. If the wave function is antisymmetric, the NO's are all complex. If the NO $X_k(\kappa)$ is associated with the occupation amplitude η_k , then in the case of an antisymmetric wave function, there will be a NO $X_k^*(\kappa)$ associated with the occupation amplitude η_k^* , i.e. the occupation amplitudes occur in conjugate pairs for an

antisymmetric wave function.

Suppose that the wave function is an S-function of the form

$$\Psi(r_1, r_2) = \sum_{L=0}^{\infty} \Psi_L(r_1, r_2) \left(\frac{2L+1}{2} \right)^{\frac{1}{2}} \frac{P_L(\cos \theta_{12})}{\pi \sqrt{8}} \quad (\text{I.14})$$

where the $P_L(\cos \theta_{12})$ are Legendre polynomials. In such a case each NO can be written as $\chi_{kLM_L}(r)$ and is $(2L+1)$ -fold degenerate with respect to the eigenvalue η_{kL} . Thus

$$\chi_{kLM_L}(r) = \chi_{kL}(r) Y_L^{M_L}(\theta, \phi) \quad (\text{I.15})$$

where $Y_L^{M_L}(\theta, \phi)$ is the L-th order spherical harmonic. The integral eigenvalue equation is thus

$$\eta_{kL} \chi_{kL}(r_1) = \int \Psi_L(r_1, r_2) \chi_{kL}(r_2) r_2^2 dr_2 \quad (\text{I.16})$$

The wave function $\Psi(r_1, r_2)$, expanded in terms of the NO's, has the form

$$\Psi(r_1, r_2) = \sum_k \eta_k \chi_k(r_1) \chi_k(r_2) \quad (\text{I.17})$$

if the wave function is symmetric, and

$$\Psi(r_1, r_2) = \sum_k \eta_k \left[\chi_k(r_1) \chi_k^*(r_2) - \chi_k^*(r_1) \chi_k(r_2) \right] \quad (\text{I.18})$$

if the wave function is antisymmetric. Since the wave function can also be expanded in terms of any suitable complete set of orthonormal functions, the NO's must be related to any such set of functions by a unitary transformation. However, depending on the nature of the wave function with respect to which the NO's are defined, the eigenvalue equation (I.9) might not yield the complete set of NO's, but only a subset of them. Suppose that there is a set of functions $g_i(\xi)$ strongly orthogonal to the wave function $\Psi(\xi_1, \xi_2)$, i.e.

$$\int \Psi(\xi_1, \xi_2) g_i(\xi_1) d\xi_1 = \int \Psi(\xi_1, \xi_2) g_i(\xi_2) d\xi_2 = 0. \quad (\text{I.19})$$

In expanding the wave function in a complete set of functions, only that part of the complete set which is orthogonal to the set of functions $g_i(\xi)$ will explicitly appear in the expansion. The missing functions can be included formally in the expansion with zero coefficient. In this sense, eq. (I.9) can be considered as defining a complete set of NO's. All of the NO's (or linear combinations of them) which are strongly orthogonal to $\Psi(\xi_1, \xi_2)$ will occur as the eigenfunctions of the zero eigenvalue. Those NO's which are associated with zero occupation amplitude have been called ¹⁹ improper NO's by Kutzelnigg. The properties of NO's associated with strongly orthogonal functions have been discussed by Arai³⁸ and by Lowdin.³⁹

APPENDIX II. PHYSICAL INTERPRETATION OF THE SELF-CONSISTENT FIELD SCHEMES

All of the N-configuration wave functions $\Psi_N(\epsilon_1, \epsilon_2)$ discussed in Section II are SCF functions since the orbitals comprising them are obtained as self-consistent solutions of coupled equations. The RHF scheme is the simplest example of a SCF scheme. The traditional interpretation of the RHF scheme is to picture each electron as moving in the average field of the other electron. As it turns out, one can interpret any of the SCF schemes discussed in Section II in terms of average fields.

Let the SCF equations, eq. (2.7), be rewritten as

$$\sum_{k=1}^N \eta_{N,k} \langle X_{N,k}(\epsilon_2) | \left[h(\epsilon_1) + \frac{1}{2} \frac{1}{r_{12}} - \epsilon_{N,k}^{(\epsilon_2)} \right] \times P(1,2) X_{N,i}(\epsilon_1) | X_{N,k}(\epsilon_2) \rangle = 0 \quad (\text{II.1})$$

for $1 \leq i \leq N$. In the N-configuration SCF model of a two-electron system each electron is allowed to occupy each of N states $X_{N,k}^{(\epsilon)}$ with a probability equal to $\eta_{N,k}^2$ since the one-particle density matrix $P_N(\epsilon_1, \epsilon_1')$ is equal to

$$P_N(\epsilon_1, \epsilon_1') = \sum_{k=1}^N \eta_{N,k}^2 X_{N,k}(\epsilon_1) X_{N,k}(\epsilon_1'). \quad (\text{II.2})$$

Consider the expression inside the brackets of eq. (II.1). The permutation operator $P(1,2)$ acts on the arguments of the functions following it prior to integration and is present to take account of electron exchange. Forgetting about the permutation operator for the moment, the rest of the expression can be considered as a one-electron Hamiltonian, $h(\kappa) + \frac{1}{2} \frac{1}{r_{12}}$, and an energy $\mathcal{E}_{N,R}^{(\kappa_2)}$ where

$$\mathcal{E}_{N,R}^{(\kappa_2)} = E_N - \mathcal{E}_{N,R}^{(\kappa_2) \text{ LOCAL}} \quad (\text{II.3})$$

with the local energy

$$\mathcal{E}_{N,R}^{(\kappa_2) \text{ LOCAL}} = \frac{X_{N,R}(\kappa_2) h(\kappa_2) X_{N,R}(\kappa_2)}{X_{N,R}(\kappa_2) X_{N,R}(\kappa_2)} \quad (\text{II.4})$$

The one-electron Hamiltonian, considered as an operator depending on \underline{r}_1 as a variable and \underline{r}_2 as a parameter, would be the Hamiltonian for the motion of an electron in the field of a unit positive charge at the origin of coordinates and a unit negative charge held fixed at \underline{r}_2 . The term $1/2$ measures the strength of the electronic interaction relative to the central field. The quantity $\mathcal{E}_{N,R}(\kappa_2)$ is the energy of the moving electron and depends parametrically on the position of the stationary electron. The actual spatial distribution of Electron 1 in the i -th state, $X_{N,i}^{(\kappa_1)}$, is obtained by quantum-mechanically averaging over all possible positions of Electron 2 in each of its possible states and then summing over all the possible states in which Electron 2 can be found, weighting each member of the

sum by the occupation amplitude associated with the particular state.

The DODS ground-state function can be transformed into the form

$$\psi_{\text{DODS}}(k_1, k_2) = N \left(\frac{1 + P(1,2)}{\sqrt{2}} \right) f(k_1) g(k_2) \quad (\text{II.5})$$

where

$$f(k) = \frac{1}{\sqrt{2}} \left[(\gamma_{\text{DODS},01})^{\frac{1}{2}} \chi_{\text{DODS},01}^{(k)} + (\gamma_{\text{DODS},02})^{\frac{1}{2}} \chi_{\text{DODS},02}^{(k)} \right] \quad (\text{II.6a})$$

and

$$g(k) = \frac{1}{\sqrt{2}} \left[(\gamma_{\text{DODS},01})^{\frac{1}{2}} \chi_{\text{DODS},01}^{(k)} - (\gamma_{\text{DODS},02})^{\frac{1}{2}} \chi_{\text{DODS},02}^{(k)} \right]. \quad (\text{II.6b})$$

The DODS equations can be written as

$$\begin{aligned} \langle g(k_2) | \left[h(k_1) + \frac{1}{2} \frac{1}{r_{12}} - \epsilon_f(k_2) \right] \\ \times \left(\frac{1 + P(1,2)}{\sqrt{2}} \right) f(k_1) | g(k_2) \rangle_{r_2} = 0 \end{aligned} \quad (\text{II.7a})$$

and

$$\begin{aligned} \langle f(k_1) | \left[h(k_2) + \frac{1}{2} \frac{1}{r_{12}} - \epsilon_g(k_1) \right] \\ \left(\frac{1 + P(1,2)}{\sqrt{2}} \right) g(k_2) | f(k_1) \rangle_{r_1} = 0 \end{aligned} \quad (\text{II.7b})$$

where

$$\epsilon_f(\kappa_2) = E_{\text{DODS}} - \frac{g(\kappa_2) h(\kappa_2) g(\kappa_2)}{g(\kappa_2) g(\kappa_2)} \quad (\text{II.8})$$

and similarly for $\epsilon_g(\kappa_1)$. The functional form of $\psi_{\text{DODS}}^{(2)}(\kappa_1, \kappa_2)$ suggests that in the DODS model one of the electrons is pulled in close to the nucleus while the other electron is pushed farther out. The permutation operator is present to take care of symmetry. Forgetting for the moment the permutation operator and the quantum-mechanical averaging in eqs. (II.7), what remains of the equations is very similar to the equations arising in the core-polarization method⁴⁰ without exchange. The DODS model can be thus interpreted as an average core-polarization method including exchange.

From the form of the DODS orbitals f and g , eqs. (II.6), and from the fact that $\eta_{\text{DODS},02}$ is a correlation occupation amplitude for the ground state (it must go to zero as $1/Z$ goes to zero), one can see why $1/\sqrt{Z}$ must be used in performing a perturbation expansion^{12,25} of the DODS function written in the form of eq. (II.5).

APPENDIX III. CONCERNING THE SIGN OF THE FIRST-ORDER NATURAL OCCUPATION AMPLITUDES

In this appendix it will be shown that all first-order natural occupation amplitudes cannot be positive. One already has the result, as shown in eq. (4.11a), that the first-order intrinsic occupation amplitude must be zero.

The first-order correlation amplitudes $\eta_{Lk}^{(1)}$, $k \geq k_L$, are given by eq. (4.26) as

$$-\eta_{Lk}^{(1)} = \frac{\langle X_{Lk}^{(0)} | V_L | X_{Lk}^{(0)} \rangle}{1 + 2 \langle X_{Lk}^{(0)} | V_L | X_{Lk}^{(0)} \rangle} \quad (\text{III.1})$$

since $E^{(0)}$ is equal to -1 for the ground state. The numerator of eq. (III.1) is $\frac{1}{\sqrt{2L+1}} \langle X_{Lk}^{(0)}(r_1) X_{Lk}^{(0)}(r_2) | \frac{r_{12}^L}{r_1^{L+1} r_2^{L+1}} | 1S(r_1) 1S(r_2) \rangle$ which is non-negative, i.e.

$$\langle X_{Lk}^{(0)} | V_L | X_{Lk}^{(0)} \rangle \geq 0. \quad (\text{III.2})$$

The denominator of eq. (III.1) can be shown to be positive by expanding the functions $X_{Lk}^{(0)}$ in terms of the complete set of hydrogenic orbitals the discrete part of which will be denoted by $\phi_{Li}(r)$, $1 \leq i < \infty$, and the continuum part by $\phi_L(r, i)$.

Thus

$$X_{Lk}^{(0)} = \sum_{i=k_L}^{\infty} C_{Lk,i} \phi_{Li}(r) + \int_0^{\infty} di C_{Lk}(i) \phi_L(r, i) \quad (\text{III.3})$$

with $k_L = 2$ for $L = 0$ and $k_L = 1$ for $L \geq 1$. Since the $X_{Lk}^{(0)}(r)$ are normalized to unity one has

$$1 = \sum_{i=k_L}^{\infty} C_{Lk,i}^2 + \int_0^{\infty} di C_{Lk}^2(i) \quad (\text{III.4})$$

and therefore

$$0 \leq C_{Lk,i}^2 \leq 1 \quad (\text{III.5a})$$

and

$$0 \leq C_{Lk}^2(i) \leq 1. \quad (\text{III.5b})$$

The denominator of eq. (III.1) is thus

$$1 + 2 \langle X_{Lk}^{(0)} | h_L | X_{Lk}^{(0)} \rangle = 1 + 2 \sum_{i=k_L}^{\infty} C_{Lk,i}^2 \left(-\frac{1}{2(L+i)^2} \right) + \int_0^{\infty} di C_{Lk}^2(i) \mathcal{E}(i) \quad (\text{III.6})$$

since

$$h_L(r) \phi_{Li}(r) = -\frac{1}{2(L+i)^2} \phi_{Li}(r). \quad (\text{III.7})$$

The quantity $\mathcal{E}(i)$ is a continuum energy and is therefore positive. Since the $C_{Lk}^2(i)$ are positive, the continuum contribution to the denominator is positive. Therefore, using eq. (III.5a),

$$1 + 2 \langle X_{Lk}^{(0)} | h_L | X_{Lk}^{(0)} \rangle \geq 1 - \sum_{i=k_L}^{\infty} \frac{1}{(L+i)^2} \quad (\text{III.8})$$

and thus, since

$$\sum_{i=k_L}^{\infty} \frac{1}{(L+i)^2} = \frac{\pi^2}{6} - \left(1 + \frac{1}{2^2} + \dots + \frac{1}{(L+\delta_{L,0})^2} \right), \quad (\text{III.9})$$

one has

$$1 + 2 \langle X_{Lk}^{(0)} | h_L | X_{Lk}^{(0)} \rangle > 0. \quad (\text{III.10})$$

Therefore, substituting eqs. (III.2) and (III.10) into eq. (III.1) yields the inequality

$$- \gamma_{Lk}^{(1)} \geq 0 \quad (\text{III.11})$$

for $k \geq k_L$. Taking into account the first-order intrinsic occupation amplitude, eq. (4.11a), gives the desired result

$$\gamma_{Lk}^{(1)} \leq 0 \quad (\text{III.12})$$

for all $k \geq 1$.

APPENDIX IV: CALCULATION OF THE MATRIX ELEMENTS

In this appendix the calculation of the matrix elements $h_{L,mn}$ and $V_{L,mn}$ occurring in eqs. (6.3) and (6.4) of Section VI will be indicated in some detail.

The associated Laguerre functions $f_{Ln}^{(r)}$ used in expanding the orbitals $X_{EHF,LK}^{(0)}$ are

$$f_{Ln}^{(r)} = 2^{3/2} \frac{n!}{(2L+n+2)!} (2r)^L L_n^{(2L+2)}(2r) e^{-r} \quad (\text{IV.1})$$

where the associated Laguerre polynomial $L_n^{(\alpha)}(r)$ is

$$L_n^{(\alpha)} = \sum_{\nu=0}^n \binom{n+\alpha}{n-\nu} \frac{(-r)^\nu}{\nu!} \quad (\text{IV.2})$$

where $\binom{n+\alpha}{n-\nu}$ is the binomial coefficient. These polynomials satisfy the differential equation⁴¹

$$r \frac{d^2 L_n^{(\alpha)}(r)}{dr^2} + (\alpha+1-r) \frac{d L_n^{(\alpha)}(r)}{dr} + n L_n^{(\alpha)}(r) = 0 \quad (\text{IV.3})$$

and the following relationships:

$$\frac{d L_n^{(\alpha)}(r)}{dr} = -L_{n-1}^{(\alpha+1)}(r), \quad (\text{IV.4a})$$

$$r \frac{d L_n^{(\alpha)}(r)}{dr} = n L_n^{(\alpha)}(r) - (n+\alpha) L_{n-1}^{(\alpha-1)}(r) \quad (\text{IV.4b})$$

and the recurrence relation

$$(n+1)L_{n+1}^{(\alpha)} = (2n+1+\alpha-r)L_n^{(\alpha)} - (n+\alpha)L_{n-1}^{(\alpha)} \quad (\text{IV.4c})$$

The orthonormality integral for the polynomials is

$$\int_0^\infty dr r^\alpha e^{-r} L_m^{(\alpha)} L_n^{(\alpha)} = \alpha! \binom{m+\alpha}{m} \delta_{m,n} \quad (\text{IV.5})$$

and their generating function is

$$\sum_{q=0}^{\infty} \omega^q L_q^{(\alpha)} = (1-\omega)^{-(\alpha+1)} e^{-r \frac{\omega}{1-\omega}} \quad (\text{IV.6})$$

The associated polynomials $L_{n+2L+2}^{(2L+2)}$ are related to the second-order Laguerre polynomials $L_n^{(2L+2)}$ used by Hirschfelder and Löwdin,²⁷ Shull and Lowdin^{14,15} and Kutzelnigg²⁸ by the relationship

$$L_{n+2L+2}^{2L+2} = (n+2L+2)! L_n^{(2L+2)} \quad (\text{IV.7})$$

for $n \geq 0$. The general relationship is

$$L_{n+\alpha}^{(\alpha)} = (-1)^\alpha (n+\alpha)! L_n^{(\alpha)} \quad (\text{IV.8})$$

The matrix element $h_{L,mn}$ is

$$h_{L,mn} = \langle f_{Lm}(r) | h_L(r) | f_{Ln}(r) \rangle \quad (\text{IV.9})$$

where

$$h_L(r) = -\frac{1}{2r} \frac{d^2(r)}{dr^2} - \frac{1}{r} + \frac{L(L+1)}{2r^2}, \quad (\text{IV.10})$$

and the matrix element $V_{L,mn}$ is

$$V_{L,mn} = \frac{1}{\sqrt{2L+1}}$$

$$\times \left\langle f_{Lm}(r_1) f_{Ln}(r_2) \left| \frac{r_1^{L+1}}{r_2^{L+1}} \right| f_{00}(r_1) \right. \\ \left. \times f_{00}(r_2) \right\rangle \quad (\text{IV.11})$$

where $f_{00}(r)$ is the 1s hydrogenic orbital.

Writing out the expression for $h_{L,mn}$ in detail one has

$$h_{L,mn} = -2N_{Lm}N_{Ln} \bar{h}_{L,mn} \quad (\text{IV.12})$$

where, after using eq. (IV.3),

$$\bar{h}_{L,mn} = \frac{1}{4} \int_0^\infty dx x^{2L+2} e^{-x} L_m^{(2L+2)}(x) L_n^{(2L+2)}(x) \\ - \int_0^\infty dx x^{2L+1} e^{-x} L_m^{(2L+2)}(x) \frac{d}{dx} L_n^{(2L+2)}(x) \quad (\text{IV.13}) \\ - (L+n) \int_0^\infty dx x^{2L+1} e^{-x} L_m^{(2L+2)}(x) L_n^{(2L+2)}(x)$$

where $x=2r$ and where

$$N_{Lm} = \sqrt{\frac{m!}{(2L+m+2)!}}. \quad (\text{IV.14})$$

Then, using eqs. (IV.4a) and (IV.5), one has

$$\begin{aligned} \bar{h}_{L,mn} = & \frac{1}{4} (2L+2)! \binom{m+2L+2}{m} \delta_{m,n} \\ & + J_{L,m,n-1} - (L+n) I_{L,mn}, \end{aligned} \quad (\text{IV.15})$$

where

$$I_{L,mn} = \int_0^\infty dx \, x^{2L+1} e^{-x} L_m^{(2L+2)}(x) L_n^{(2L+2)}(x) \quad (\text{IV.16})$$

and

$$J_{L,mn} = \int_0^\infty dx \, x^{2L+1} e^{-x} L_m^{(2L+2)}(x) L_n^{(2L+3)}(x). \quad (\text{IV.17})$$

The integrals $I_{L,mn}$ are easily calculated using the generating function of the polynomials (IV.6). The method used below is the same method used by Hirschfelder and Löwdin.²⁷ Integrating the generating function appropriately, one has

$$\sum_{p,q=0}^{\infty} \mu^p \nu^q I_{L,pq} = \frac{(2L+1)!}{\left[\frac{\mu}{1-\mu} + \frac{\nu}{1-\nu} + 1 \right]^{(2L+2)}}. \quad (\text{IV.18})$$

The integral $I_{L,mn}$ is obtained from eq. (IV.18) by differentiating both sides m -times with respect to μ and n -times with respect to

ν and then setting both μ and ν equal to zero. Thus, one obtains for $m \geq n$,

$$I_{L,mn} = \frac{1}{m!n!} \sum_{i=0}^n \binom{m}{i} \binom{n}{i} (m-i)! \\ \times (\eta-i)! (2L+1+i)! (i)!$$

(IV.19)

which can be summed to

$$I_{L,mn} = \sum_{i=0}^n \frac{(2L+1+i)!}{(i)!}.$$

(IV.20)

A similar treatment of the integral $J_{L,mn}$ gives, for $m \geq n$,

$$J_{L,mn} = \sum_{i=0}^n \frac{(2L+1+i)!}{(i)!} (\eta-i+1).$$

(IV.21)

Substituting eqs. (IV.20) and (IV.21) into eq. (IV.15) and using the relations⁴²

$$\sum_{i=0}^n \frac{(2L+1+i)!}{(i)!} = \frac{(2L+2+\eta)!}{(2L+1)(\eta)!}$$

(IV.22)

and

$$\sum_{i=0}^n \frac{(2L+1+i)!}{(i)!} (i) = \frac{(2L+2+\eta)!}{(2L+3)(\eta-1)!}$$

(IV.23)

one obtains, for $m \geq n$, the following expression for $h_{L,mn}$

$$h_{L,mn} = \sqrt{\frac{m! (2L+2+n)!}{n! (2L+2+m)!}} \left[-\frac{1}{2} \delta_{mn} + \frac{L}{(L+1)} + \frac{2n}{(2L+3)} \right] \quad (\text{IV.24})$$

The integral $V_{L,mn}$ can be written as

$$V_{L,mn} = \frac{N_{Lm} N_{Ln}}{\sqrt{2L+1}} \left[K_{m,n}^{(2L+2)} + K_{n,m}^{(2L+2)} \right] \quad (\text{IV.25})$$

where

$$K_{m,n}^{(\alpha)} = \int_0^\infty dx_1 x_1^\alpha e^{-x_1} L_m^{(\alpha)}(x_1) \\ \times \int_{x_1}^\infty dx_2 x_2 e^{-x_2} L_n^{(\alpha)}(x_2). \quad (\text{IV.26})$$

Using the recurrence relation, eq. (IV.4c), one can write

$$K_{m,n}^{(\alpha)} = (n+1) A_{m,n+1}^{(\alpha)} \\ + (2n+1+\alpha) A_{m,n}^{(\alpha)} \\ - (n+\alpha) A_{m,n-1}^{(\alpha)} \quad (\text{IV.27})$$

where

$$A_{ms}^{(\alpha)} = \int_0^\infty dx_1 x_1^\alpha e^{-x_1} L_m^{(\alpha)}(x_1) \int_{x_1}^\infty dx_2 e^{-x_2} L_s^{(\alpha)}(x_2). \quad (\text{IV.28})$$

The integrals $A_{ms}^{(\alpha)}$ can be calculated by using the generating function, eq. (IV.6), in much the same way as for the integrals $I_{L,mn}$ and $J_{L,mn}$. One thus has

$$\sum_{p,q=0}^{\infty} \mu^p \sigma^q A_{pq}^{(\alpha)} = \alpha! \frac{(1-\sigma)}{(2-\mu\sigma)^{(\alpha+1)}} \quad (\text{IV.29})$$

which yields

$$A_{ms}^{(\alpha)} = \frac{(\alpha+m+s-1)! (\alpha+m-s)}{m! s! 2^{(\alpha+m+s+1)}} \quad (\text{IV.30})$$

giving

$$K_{mn}^{(\alpha)} = \frac{(\alpha+m+n-2)!}{m! n! 2^{(\alpha+m+n+2)}} \times \left[\begin{aligned} & -(\alpha+m-n-1)(\alpha+m+n)(\alpha+m+n-1) \\ & + (\alpha+m-n)(\alpha+m+n-1)(2n+\alpha+1) \\ & - 4(\alpha+m-n+1)(n+\alpha)n \end{aligned} \right] \quad (\text{IV.31})$$

Substituting eq. (IV.31) into eq. (IV.25) gives

$$V_{L,mn} = \sqrt{2L+1} (m+n+2)! \times \left[\frac{2(L+1)(2L+5) + (m+n) - (m-n)^2}{2^{(m+n+2L+3)} m! n! \times} \right] \times \sqrt{(2L+m+2)! (2L+n+2)!} \quad (\text{IV.32})$$

Some of the above matrix elements are zero. If they are denoted by

$V_{L, m_0 n_0}$, then the indices m_0 and n_0 must be related by the equation

$$2(2L+5)(L+1) + m_0 + n_0 - (m_0 - n_0)^2 = 0 \quad (\text{IV.33})$$

or by

$$n_0 = \frac{1}{2} \left[(2m_0 + 1) + \sqrt{8m_0 + 8L(2L+7) + 4} \right] \quad (\text{IV.34})$$

The above two equations were obtained by setting the numerator of the term in square brackets of eq. (IV.32) equal to zero.

The following schemes were used for calculating the integrals $h_{L, mn}$ and $V_{L, mn}$ recursively by computer. For the case of $L = 0$, the computer was given the value

$$h_{0, 11} = \frac{1}{6} \quad (\text{IV.35})$$

which was used to calculate the diagonal elements $h_{0, nn}$ by the formula

$$h_{0, nn} = h_{0, n-1, n-1} + \frac{2}{3} \quad (\text{IV.36})$$

and these were used to calculate the elements $h_{0, n+1, n}$ by the formula

$$h_{0, n+1, n} = \left(\frac{1}{2} + h_{0, nn} \right) \sqrt{\frac{n+1}{n+3}} \quad (\text{IV.37})$$

which were then used in the formula, $m \geq n+2$

$$h_{0,mn} = h_{0,m-1n} \sqrt{\frac{m}{m+2}} \quad (\text{IV.38})$$

From eqs. (IV.32) and (IV.34) one can define the following recursive scheme for calculating the integrals $V_{0,mn}$:

$$V_{0,11} = \frac{1}{8} \quad (\text{IV.39})$$

$$V_{0,n1} = V_{0,n-1n-1} \frac{(2n-1)(5+n)}{2(n+2)(4+n)}, \quad (\text{IV.40})$$

$$V_{0,n+1,n} = V_{0,n1} \frac{(2n+1)}{2\sqrt{(n+1)(n+3)}}, \quad (\text{IV.41})$$

for $m \geq n+2$

$$V_{0,mn} = V_{0,m-1n} \frac{(m+n)}{2\sqrt{m(m+2)}} \times \left[1 + \frac{2(n-m+1)}{9+m+n-(n-m+1)^2} \right] \quad (\text{IV.42})$$

and for $m_0 > n_0$

$$\begin{aligned}
 V_{0, m_0+1} \eta_0 &= V_{0, m_0-1} \eta_0 \\
 &\times \frac{(m_0+n_0+1)(m_0+n_0)}{4\sqrt{(m_0+3)(m_0+2)(m_0+1)m_0}} \\
 &\times \left(\frac{11+m_0+n_0-(m_0-n_0+1)^2}{9+m_0+n_0-(m_0-n_0+1)^2} \right)
 \end{aligned}
 \tag{IV.43}$$

where, from eq. (IV.33) or (IV.34), the pairs of values (m_0, n_0) are (5,1), (10,5), (16,10), (23,16), (31,23), (40,31), etc.

For computational purposes the matrix elements $h_{L,mn}$ and $v_{L,mn}$ for $L \geq 1$ were relabeled as

$$h_{L,mn} = h_{L,m-1} \eta-1 \tag{IV.44}$$

and

$$v_{L,mn} = v_{L,m-1} \eta-1 \tag{IV.45}$$

for $m, n \geq 1$. The following recursive scheme was used to calculate the integrals $h_{L,mn}$, $L \geq 1$:

$$h_{L,11} = \frac{(L-1)}{2(L+1)}, \tag{IV.46}$$

$$h_{L,nn} = h_{L,n-1,n-1} + \left(\frac{2}{2L+3}\right), \quad (\text{IV.47})$$

$$h_{L,n+1,n} = \left(\frac{1}{2} + h_{L,nn}\right) \sqrt{\frac{n}{2L+n+2}} \quad (\text{IV.48})$$

and for $m \geq n+2$

$$h_{L,mn} = h_{L,m-1,n} \sqrt{\frac{m-1}{2L+m+1}}. \quad (\text{IV.49})$$

The following recursive scheme was used to obtain the matrix elements

$v_{L,mn}$, $L \geq 1$:

$$v_{L,11} = \frac{(2L+5)}{2(2L+3)\sqrt{2L+1}}, \quad (\text{IV.50})$$

$$v_{L,nn} = v_{L,n-1,n-1} \frac{(L+n-1)(2L+2n-3)}{2(2L+n+1)(n-1)}$$

$$\times \left(\frac{(L+1)(2L+5)+n-1}{(L+1)(2L+5)+n-2} \right),$$

(IV.51)

$$U_{L,n+1,n} = U_{L,n,n} \frac{2L+2n-1}{2\sqrt{n(2L+n+2)}}, \quad (\text{IV.52})$$

for $m \geq n+2$

$$U_{L,m,n} = U_{L,m-1,n} \frac{(m+n+2L-2)}{2\sqrt{(m-1)(2L+m+1)}}, \quad (\text{IV.53})$$

$$\frac{2(L+1)(2L+5)+m+n-2-(m-n)^2}{2(L+1)(2L+5)+m+n-3-(m-n-1)^2}$$

and for $m_0 > n_0$

$$U_{L,m_0+1,n_0} = U_{L,m_0-1,n_0}$$

$$\times \frac{(2L+m_0+n_0-1)(2L+m_0+n_0-2)}{4\sqrt{(m_0-1)m_0(2L+m_0+1)(2L+m_0+2)}}$$

$$\times \frac{2(L+1)(2L+5)+m_0+n_0-7-(m_0-n_0+1)^2}{2(L+1)(2L+5)+m_0+n_0-3-(m_0-n_0-1)^2}$$

(IV.54)

where the values for m_0 and n_0 are listed in Table VII.

TABLE VII
Some Values for m_o and n_o

L	(m_o, n_o)				
1	(8, 2)	(15, 8)	(23, 15)	(32, 23)	etc.
2	(10, 2)	(19, 10)	(29, 19)	(40, 29)	etc.
3	(12, 2)	(23, 12)	(35, 23)	etc.	
4	(14, 2)	(27, 14)	etc.		
etc.					

The recursive schemes defined above turned out to be quite accurate. The computer was given a starting value accurate to ten significant figures. After using the recursive schemes forty times, the matrix elements were still accurate to ten significant figures. The recursive schemes are much easier to use than the more general summation expressions developed by Jones and Brooks.⁴³

APPENDIX V: COEFFICIENTS OF SOME ZERO-ORDER BASIC EXTENDED HARTREE-FOCK ORBITALS

In this appendix the expansion coefficients for several of the forty term wave functions $\tilde{X}_{EHF, L k_L}^{(0)}$ will be listed. Only those wave functions are considered which are associated with the values $\tilde{E}_{EHF, L k_L}^{(2)}$. Each coefficient $\tilde{C}_{L k_L, n}$ is a function of the parameter $\mu_{L k_L}^{(1)}$ and is listed for the optimal value $\tilde{\mu}_{EHF, L k_L}^{(1)}$ of each parameter. It will be recalled from Section VI, eq. (6.1) and (6.2), that the orbitals $\tilde{X}_{EHF, L k_L}^{(0)}$ were expanded as

$$\tilde{X}_{EHF, L k_L}^{(0)} = \sum_{n=k_L-1}^{38+k_L} \tilde{C}_{L k_L, n} f_{Ln}^{(n)} \quad (V.1)$$

where the functions $f_{Ln}^{(n)}$ are the associated Laguerre functions

$$f_{Ln}^{(n)} = 2^{3/2} \frac{n!}{\sqrt{(2L+n+2)!}} (2r)^L L_n^{(2L+2)} e^{-r} \quad (V.2)$$

The coefficients of the functions $\tilde{X}_{EHF, 02}^{(0)}$, $\tilde{X}_{EHF, 03}^{(0)}$, $\tilde{X}_{EHF, 04}^{(0)}$ and $\tilde{X}_{EHF, 05}^{(0)}$ are listed in Table VIII; the coefficients of the functions $\tilde{X}_{EHF, 11}^{(0)}$, $\tilde{X}_{EHF, 12}^{(0)}$, $\tilde{X}_{EHF, 13}^{(0)}$ and $\tilde{X}_{EHF, 14}^{(0)}$ are listed in Table IX; and the coefficients of the functions

$$\tilde{X}_{EHF, 21}^{(0)}, \tilde{X}_{EHF, 31}^{(0)}, \tilde{X}_{EHF, 41}^{(0)}, \\ \tilde{X}_{EHF, 51}^{(0)}, \tilde{X}_{EHF, 61}^{(0)}, \text{ and } \tilde{X}_{EHF, 71}^{(0)} \quad \text{are}$$

listed in Table X. All numbers have been rounded off to the given values. The value -0.00000 means that the coefficient is less than the number -0.000005.

TABLE VIII

Coefficients of Some S-Type Zero-Order EHF Orbitals

n	$c_{02,n}$	$c_{03,n}$	$c_{04,n}$	$c_{05,n}$
1	0.970972	-0.496560	0.34467	-0.248
2	0.227633	0.472334	-0.45212	0.446
3	-0.009084	0.584890	-0.24765	0.143
4	-0.052732	0.377988	0.16092	-0.206
5	-0.021704	0.149303	0.41057	-0.279
6	-0.024500	-0.001995	0.44938	-0.267
7	-0.011578	-0.072325	0.35011	0.101
8	-0.004181	-0.087957	0.20033	0.286
9	-0.000610	-0.075656	0.06069	0.374
10	0.000791	-0.053861	-0.04014	0.367
11	0.001126	-0.032601	-0.09678	0.291
12	0.001016	-0.016010	-0.11645	0.182
13	0.000770	-0.004855	-0.11079	0.071
14	0.000528	0.001645	-0.09114	-0.023
15	0.000335	0.004751	-0.06631	-0.090
16	0.000198	0.005673	-0.04210	-0.284
17	0.000110	0.005358	-0.02168	-0.141
18	0.000055	0.004468	-0.00629	-0.135
19	0.000023	0.003412	0.00409	-0.116
20	0.000006	0.002416	0.01017	-0.091
21	-0.000003	0.001584	0.01292	-0.064
22	-0.000006	0.000945	0.01334	-0.038
23	-0.000006	0.000487	0.01228	-0.017
24	-0.000006	0.000180	0.01043	-0.000
25	-0.000005	-0.000010	0.00828	0.012
26	-0.000003	-0.000113	0.00616	0.019
27	-0.000002	-0.000160	0.00427	0.023
28	-0.000002	-0.000171	0.00269	0.024
29	-0.000001	-0.000161	0.00145	0.023
30	-0.000001	-0.000140	0.00054	0.020
31	0.000000	-0.000113	-0.00010	0.017
32	-0.000000	-0.000087	-0.00050	0.013
33	-0.000001	-0.000065	-0.00072	0.010
34	0.000001	-0.000047	-0.00081	0.007
35	-0.000000	-0.000033	-0.00081	0.004
36	0.000000	-0.000021	-0.00077	0.001
37	0.000001	-0.000011	-0.00068	-0.001
38	0.000000	-0.000002	-0.00061	-0.003
39	0.000000	-0.000005	-0.00054	-0.004
40	-0.000001	0.000014	-0.00053	-0.007

TABLE IX

Coefficients of Some P-Type Zero-Order EHF Orbitals

n	$c_{11,n}$	$c_{12,n}$	$c_{13,n}$	$c_{14,n}$
0	0.896143	-0.620	-0.447	-0.342
1	0.421112	0.203	0.347	0.385
2	0.135407	0.503	0.387	0.266
3	0.019260	0.455	0.082	-0.087
4	-0.015166	0.295	-0.217	-0.286
5	-0.018910	0.143	-0.374	-0.265
6	-0.014098	0.041	-0.392	-0.103
7	-0.008626	-0.015	-0.323	0.092
8	-0.004595	-0.037	-0.218	0.247
9	-0.002106	-0.040	-0.006	0.330
10	-0.000743	-0.033	-0.035	0.341
11	-0.000081	-0.024	0.020	0.299
12	0.000187	-0.016	0.050	0.226
13	0.000257	-0.009	0.061	0.144
14	0.000237	-0.004	0.060	0.066
15	0.000188	-0.001	0.051	0.003
16	0.000136	0.001	0.040	-0.042
17	0.000092	0.001	0.028	-0.069
18	0.000060	0.002	0.180	-0.082
19	0.000034	0.002	0.010	-0.082
20	0.000021	0.001	0.004	-0.076
21	0.000011	0.001	-0.001	-0.063
22	0.000004	0.001	-0.003	-0.049
23	0.000001	0.001	-0.004	-0.035
24	-0.000001	0.000	-0.005	-0.022
25	-0.000003	0.000	-0.004	-0.012
26	-0.000001	0.000	-0.004	-0.004
27	-0.000001	0.000	-0.003	0.002
28	-0.000000	0.000	-0.003	0.006
29	-0.000000	-0.000	-0.002	0.009
30	-0.000000	-0.000	-0.001	0.010
31	-0.000000	-0.000	-0.001	0.010
32	0.000001	-0.000	-0.001	0.009
33	-0.000000	-0.000	-0.000	0.008
34	-0.000001	-0.000	-0.000	0.007
35	-0.000000	-0.000	0.000	0.005
36	-0.000001	-0.000	0.000	0.004
37	0.000001	-0.000	0.000	0.002
38	-0.000000	-0.000	0.000	0.001
39	-0.000000	-0.000	0.001	-0.000

TABLE X

Coefficients of Some L-Type Zero-Order EHF Orbitals

n	$c_{21,n}$	$c_{31,n}$	$c_{41,n}$	$c_{51,n}$	$c_{61,n}$	$c_{71,n}$
0	0.60534	0.31872	0.1369	0.0497	0.016	0.004
1	0.58921	0.45227	0.2484	0.1077	0.039	0.012
2	0.43326	0.48193	0.3353	0.1726	0.071	0.025
3	0.26960	0.44041	0.3863	0.2347	0.110	0.043
4	0.14467	0.36240	0.0401	0.2866	0.152	0.065
5	0.06404	0.27452	0.3852	0.3233	0.194	0.092
6	0.01845	0.19308	0.3483	0.3430	0.232	0.121
7	-0.00377	0.12589	0.2991	0.3462	0.264	0.151
8	-0.01223	0.07499	0.2454	0.3352	0.288	0.190
9	-0.01350	0.03914	0.1930	0.3130	0.302	0.208
10	-0.01161	0.01567	0.1454	0.2831	0.308	0.232
11	-0.00876	0.00155	0.1048	0.2485	0.315	0.251
12	-0.00601	-0.00601	0.0716	0.2123	0.295	0.266
13	-0.00378	-0.00924	0.0458	0.1766	0.278	0.275
14	-0.00215	-0.00984	0.0266	0.1430	0.257	0.278
15	-0.00106	-0.00901	0.0129	0.1127	0.234	0.277
16	-0.00037	-0.00753	0.0036	0.0862	0.208	0.271
17	0.00001	-0.00588	-0.0022	0.0638	0.182	0.261
18	0.00021	-0.00433	-0.0056	0.0453	0.156	0.247
19	0.00028	-0.00301	-0.0071	0.0305	0.132	0.231
20	0.00028	-0.00195	-0.0074	0.0191	0.109	0.213
21	0.00025	-0.00116	-0.0071	0.0104	0.089	0.194
22	0.00020	-0.00059	-0.0062	0.0041	0.071	0.174
23	0.00016	-0.00021	-0.0052	-0.0002	0.055	0.155
24	0.00011	0.00003	-0.0042	-0.0030	0.042	0.135
25	0.00008	0.00017	-0.0032	-0.0047	0.030	0.117
26	0.00005	0.00023	-0.0024	-0.0055	0.021	0.100
27	0.00003	0.00025	-0.0017	-0.0057	0.014	0.084
28	0.00002	0.00024	-0.0011	-0.0055	0.008	0.070
29	0.00001	0.00022	-0.0007	-0.0050	0.004	0.057
30	0.00000	0.00018	-0.0003	-0.0044	0.001	0.046
31	-0.00000	0.00015	-0.0001	-0.0038	-0.002	0.036
32	-0.00000	0.00012	0.0000	-0.0031	-0.003	0.028
33	-0.00000	0.00009	0.0001	-0.0025	-0.004	0.021
34	-0.00000	0.00006	0.0002	-0.0019	-0.005	0.015
35	-0.00000	0.00004	0.0002	-0.0014	-0.005	0.010
36	-0.00000	0.00003	0.0002	-0.0010	-0.005	0.006
37	-0.00000	0.00004	0.0002	-0.0007	-0.005	0.003
38	-0.00000	-0.00000	0.0003	-0.0004	-0.005	-0.000
39	-0.00000	-0.00001	0.0003	-0.0001	-0.005	-0.003

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